Department of Chemical Engineering

Quantification of Chlorine in Solid Fuels and Its Release Behaviour During Pyrolysis

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Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: ……

Date: ……...…….

To my beloved family

ABSTRACT

Coal plays a vital role in primary energy supply in Australia and ~70% electricity is produced by coal-based power generation in 2012. Coal is expected to contribute significantly to Australia's energy mix in the foreseeable future. However, coal-based power generation faces two key challenges: depleting coal reserves and detrimental environmental impacts. Therefore, renewable energy sources, particularly biomass, are expected to play a significant role in the nation's future energy mix. In Australia, mallee biomass is grown as a part of strategy to combat dry land salinity in the wheat belt regions. Mallee biomass, as a byproduct of managing dry land salinity, is a renewable second-generation lignocelluloses feedstock. Its production is economic, of large scale, and with low energy and carbon footprints. Therefore, mallee biomass and its derived fuels are expected to play a significant role in energy security and sustainable development of rural and regional Australia.

Biomass combustion and co-firing with coal are mature technologies for power generation. However, the presence of Chlorine (Cl) in biomass causes corrosion and fouling during combustion process, leading to unexpected shutdown of power generation plants and thereby significant economic loss. In addition, Cl is also responsible for various environmental problems such as particulate matter emission, chloromethane emission, and dioxin/furan emission. Understanding the behavior and transformation of Cl during combustion is thus important however complicated due to the complex fuel pyrolysis chemistry. Therefore, Cl release and transformation during biomass pyrolysis were investigated in past decade, aiming at discovering essential knowledge for understanding the behavior of Cl during combustion and co-firing. In addition, good understanding of Cl release and transformation during biomass pyrolysis is also essential to improving fuel quality of derived bio-oil and bio-char products.

Despite of the progress made in the field of Cl release and transformation during

biomass pyrolysis, at least three significant research gaps exist due to the inaccurate quantification of Cl in biomass and the complexity of biomass structure. First, current prevailing combustion-based methods are not capable of accurately quantifying Cl in biomass due to incomplete biomass combustion and/or failure to capture all the released Cl. Second, it is also unclear that how Cl is released during biomass pyrolysis at low temperature (e.g., <400 °C). Third and last, the effects of reactor configurations on the Cl release as well as its distribution in pyrolysis products are poorly understood.

To fill these research gaps, the research program of this PhD thesis has carried out a systematical investigation focusing on the following specific objectives: (1) developing an accurate universal method for Cl quantification; (2) understanding Cl release mechanisms during biomass pyrolysis at low temperatures via using sodium chloride (NaCl) loaded cellulose a model compound; and (3) studying the release of Cl and its distribution among pyrolysis products during the pyrolysis of biomass under various reactor configurations. These objectives have been successfully achieved in this PhD study, which are briefly summarized as follows.

First, a new method for quantifying total Cl in low-rank solid fuels such as biomass and brown coal is developed. It is a two-step method that separates fuel Cl into Cl released in volatiles and that retained in char via slow pyrolysis at 500 °C. The Cl in volatiles is converted to gaseous chloride (e.g., HCl) via in situ volatiles combustion at 950 °C, followed by subsequent collection and quantification. The Cl in char is quantified via conventional Eschka method. The total Cl content in fuel is then calculated as the sum of the Cl in volatiles and that in char. The method is validated using five standard samples (i.e., a high-purity polyvinyl chloride sample, an inorganic-free cellulose char, and three NaCl-loaded cellulose chars of different Cl-loading levels). The two-step method was then used to quantify the Cl contents in three typical low-rank solid fuels (i.e., a mallee bark, a brown coal, and a water-washed brown coal), benchmarking against those analyzed using the

conventional water-washing and Eschka methods. The results suggest that the water-washing method gives similar Cl content in the bark compared to that from the two-step method because all Cl in the bark is water-soluble. However, the water-washing method substantially underestimates Cl content in the brown coal due to the presence of water-insoluble Cl. The conventional Eschka method is capable of quantifying Cl in the brown coal. However, it substantially underestimates Cl content in the bark due to the loss of Cl during Eschka combustion. It is therefore noted that in using the two-step method, the choice of 500 °C as the pyrolysis temperature is essential.

Second, in order to address the disadvantages (e.g. long analysis time) of the two-step method, an improved Eschka method has then been developed. Conventional Eschka method is a standard method for the determination of Cl in solid fuels. However, the method significantly underestimates the Cl content in some low-rank solid fuels (e.g., mallee bark) as due to the escape of Cl with flue gas of the Eschka combustion process. The improved Eschka method is developed to recover the escaped Cl in the flue gas via converting it into HCl (g) by flue gas re-combustion for capture and quantification. The experimental results have demonstrated that the improved Eschka method can accurately quantify Cl in a range of solid fuels studied (i.e., a mallee bark, a Victorian brown coal, a sub-bituminous coal, an anthracite coal, and a polyvinyl chloride), with a small relative standard error (±2%) and a low limit of quantification (0.015 mg/g fuel, dry basis) under present experimental configurations.

Third, efforts were made to study the Cl release behavior during slow pyrolysis of NaCl-loaded cellulose in the temperature range of 150−400 °C, providing new data to better understand the low-temperature release of Cl during biomass pyrolysis. The results show that the form and amount of Cl released during the slow pyrolysis of the NaCl-loaded cellulose strongly depends on temperature. At temperatures below 300 °C, Cl is released mainly as HCl (g), while the release of tar-Cl is clearly

evidenced at 350 °C or higher. The release of both HCl (g) and total Cl (including gaseous HCl and tar Cl) begins at 200 °C, reaches the corresponding maximum values (~53% for HCl and ~71% for total Cl) at 350 °C, and then levels off with further increasing temperature to 400 °C. The amount of organically bound Cl in solid residues after pyrolysis also increases from ~6% at 150 °C to ~36% at 300 °C, expressed as% of Cl in solid residues. Further increasing temperature to 350−400 °C leads to the depletion of organically-bound Cl in the solid residues. Our data clearly demonstrate that interactions between Cl and cellulose organic structure are responsible for the release of HCl (g) and tar Cl during biomass pyrolysis.

Fourth and last, mallee bark (75–150 μm) was pyrolyzed at 400–900 °C under various conditions to investigate Cl release and distribution among char, tar, and gas. In a fixed-bed pyrolysis reactor, the release of Cl is insensitive to pyrolysis temperature between 400 and 900 °C, with Cl completely released with volatiles (~ 77% in tar and ~23% in gas). In a drop-tube/fixed-bed reactor, under continuous feeding, the amount of Cl released at 400 °C is similar to that in the fixed-bed reactor. However, Cl retention in char increases with temperature, reaching a maximum at 600 °C (~42%), and then decreases with further temperature increases (e.g., only ~6% at 900 °C). The results confirm that volatile–char interactions also play important roles in Cl release and distribution among products during biomass pyrolysis and that Cl in char is thermally unstable at elevated temperatures. Quantification of Cl in tar was then carried out experimentally via in situ combustion of biomass volatiles produced using a two-column pyrolysis/combustion reactor. The results confirm the presence of substantial organically bounded Cl in tar. The mass balances of Cl in char, tar, and gas achieve ~100% closure during biomass pyrolysis in the fixed-bed reactor between 400 and 900 °C, as well as that during biomass pyrolysis in the drop-tube/fixed-bed reactor below 600 °C. However, at temperatures >600 °C, 100% Cl mass balance cannot be achieved during in situ combustion of volatiles and the data suggest that some Cl react with inorganic species (e.g., Na and K) in the gaseous phase to form alkali chlorides, which are deposited on the reactor wall.

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LIST OF AWARDS AND PUBLICATIONS

Awards

1. **Chancellor letter of commendation** for significant contribution to the field of knowledge.

2. Finalist from Curtin University in **JCEC (WA)'s Inaugural Postgraduate Research Excellence Award**, organized by Engineers Australia, 2014.

Journal Papers

1. **Rahim, M. U.**; Gao, X.; Garcia-Perez, M.; Li, Y.; Wu, H., Release of Chlorine during Mallee Bark Pyrolysis. Energy & Fuels 2012, 27, (1), 310-317.

2. **Rahim, M. U.**; Gao, X.; Wu, H., A Method for the Quantification of Chlorine in Low-Rank Solid Fuels. Energy & Fuels 2013, 27, (11), 6992-6999.

3. Gao, X.; **Rahim, M. U.**; Chen, X.; Wu, H., Significant contribution of organically-bound Mg, Ca, and Fe to inorganic PM10 emission during the combustion of pulverized Victorian brown coal. Fuel 2014, 117, Part A, 825-832.

4. **Rahim, M. U.**; Gao, X.; Wu, H., Release of Chlorine from the Slow Pyrolysis of NaCl-loaded Cellulose at Low Temperatures. Accepted in "Proceedings of the Combustion Institute" on 5 December 2013, in press.

5. **Rahim, M. U.**; Gao, X.; Wu, H., Determination of chlorine in solid fuels using and improved Eschka method. Fuel 2014, 129, 314-317.

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CHAPTER 1 INTRODUCTION

1.1 Background and Motive

Global energy demand is increasing due to improving living standards and growing world population.[1-3] Fossil fuels are currently supplying 82% of world primary energy and they are expected to contribute 76% of this energy even by 2035.[3] However, fossil fuels have limited supply and devastating environmental impacts. Strategies to diversify energy sources and address environmental impacts of fossil fuels not only include technological improvements in fossil fuel consumption but also comprise on probing and developing alternative sources of energy which can lead to sustainable development. Biomass and its derived fuels are significant sources of energy and supplied approximately 10% world primary energy in 2011.[4] However, previous reports suggest that biomass as energy feedstock has even more potential to contribute in global energy supply.[5-7]

Mallee biomass is a major biomass energy source in Western Australia (WA) and includes several species of genus *Eucalyptus* which are present in the native flora.[8] Mallee *Eucalyptus* consists of multibranched species with strong root-stocks short trees or bushes which can be harvested on short coppice cycle.[9] Deep rooted structure allows mallee species to coppice quickly after harvest thereby making harvest cycle as short as 2-5 years.[10] These species are harvested to manage dry land salinity in low to medium rainfall (300−600 mm mean annual rainfall) wheat belt region of Western Australia.[9] Since 1990, more than 30 million trees have already been planted across WA to combat dryland salinity.[11] Mallee trees are cultivated in the form of belts in order to capture additional water.[7] The area covered by mallee tress is less than 10% of the total farm.[8, 9, 12] This cultivation arrangement not only allows mallee tress to avoid competition with food crop but also complement the overall agriculture system. Mallee biomass can provide additional environmental benefits like limiting nutrient discharge and corrosion, biodiversity protection,

provision of shelter, and carbon sequestration. Moreover, mallee biomass production in WA is nearly carbon neutral.[13] Apart from the environmental benefits of mallee biomass, it can play a significant role in the sustainable energy security of Western Australia. It is estimated that mallee biomass can potentially supply 10 million dry tons of biomass per year and provide the feedstock to sustain large-scale industries.[10] Economic value of mallee biomass also provides an economic diversification opportunity for the farmers. A dedicated study on mallee biomass suggests that it's production achieves strong energy gain i.e. an energy ratio of 41.7 and an energy productivity of 206.3 GJ/(ha year). [8]

Power generation by direct combustion of biomass is a developed technology.[14, 15] However, biomass based power generation faces challenges of expensive biomass supply chain, low energy and bulk density of biomass, poor grindability, and high inorganic contents including alkali and alkaline earth metals (AAEM) and Chlorine (Cl).[16-19,] These fuel properties limit the application of biomass as a feedstock for power generation and efforts are already underway to convert biomass into biochar or bioslurry for subsequent power generation application purposes.[18, 20-24] Pyrolysis of mallee biomass can provide biochar and bioslurry with tailor made properties depending upon the ultimate use of biomass. Cl present in various component of biomass releases during combustion and gasification processes and create operational challenges including corrosion and fouling problems in the thermochemical facility.[25, 26] It is also known to cause detrimental environmental effects like particulate matter, chloromethane, as well as dioxins and furans emission. Therefore it is important to understand the release behavior of Cl during pyrolysis of various biomass components under various reactor configurations.

Release of Cl during coal pyrolysis has been well documented[27, 28] whereas Cl behaviour during biomass pyrolysis is relatively less understood.[29] Development of thorough understanding of Cl release behaviour during pyrolysis face two key challenges. Firstly, Cl quantification methods generally applied on biomass are

contextualized from coal which might not be able to quantify Cl accurately. Combustion based methods are more commonly employed for Cl determination in coal and biomass including Eschka method, bomb combustion method, and direct combustion method (See table 2-1). These methods face challenges like incomplete combustion in bomb combustion, release of Cl in forms other than HCl for Eschka combustion and recovery of Cl from salts deposits in high temperature combustion method. Therefore, it is essential to develop an accurate universal Cl quantification method. Secondly, low temperature Cl release behaviour during biomass pyrolysis is still understudy and several mechanisms have been proposed (See table 2-2).

Despite the fact that significant progress is made in understanding the release behaviour of Cl during biomass pyrolysis, still several research gaps exist in this area. For instance, an accurate universal method for Cl quantification needs to be developed which is fundamental requirement in understanding the release behaviour of Cl. Secondly, low temperature Cl releases mechanism during biomass pyrolysis needs to be explained. Thirdly, it is important to study the effect of reactor configuration on Cl release behaviour during pyrolysis. This study aims to address these fundamental research gaps in order to improve the understanding of Cl release during pyrolysis and provide essential knowledge for practical implications.

1.2 Scope and Objectives

To fill the three research gaps identified in Section 1.1, this study aims to provide fundamental understanding on the quantification of Cl in biomass and its release behavior during pyrolysis. The details objectives of this study include:

1. To develop a universal method for Cl quantification in solid fuels in order to address the limitations of combustion based Cl quantification methods.

2. To systematically investigate into the release of Cl from the slow pyrolysis of a model compound at low temperatures, aiming at providing new data for

better understanding on the low-temperature Cl release during biomass pyrolysis.

3. To study the release behaviour of Cl during the pyrolysis of mallee bark under a wide range of temperatures and various reactor configurations.

1.3 Thesis Outlines

There are 8 chapters in this thesis. Each chapter is listed below and thesis structure is schematically shown in thesis map (See Figure 1-1)

- Chapter 1 presents background and objectives of present research.
- Chapter 2 reviews the relevant literature on Cl occurrence and release during pyrolysis and highlights the research gaps and determines specific research objectives.
- Chapter 3 summarizes the experimental and analytical methodologies applied to achieve research objectives.
- Chapter 4 provides a novel method for the quantification of Cl in low rank solid fuels.
- Chapter 5 delivers an improved Eschka combustion method for Cl quantification with aim to achieve ease of operation during testing.
- Chapter 6 offers insights into the release of Cl from the slow pyrolysis of NaCl-loaded cellulose at low temperatures.
- Chapter 7 demonstrates release behavior of Cl during Mallee bark pyrolysis under various reactor configurations.
- Chapter 8 concludes this study and presents recommendations for future work.

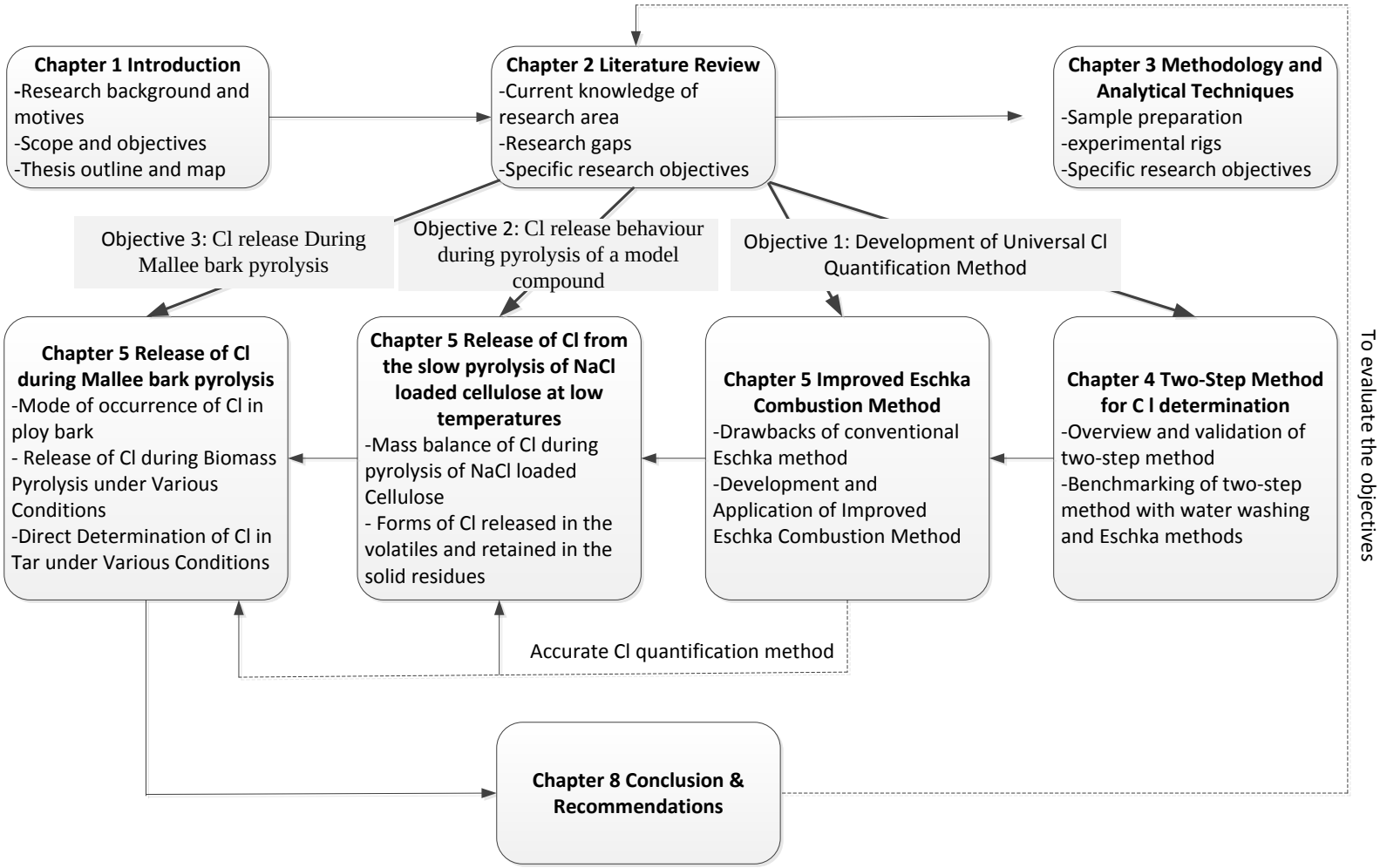

Figure 1-1: Thesis Map

CHAPTER 2 LITERATURE REVIEW

2.1 Significance of Cl

Cl in coal and biomass has attracted attention due to its operational and environmental challenges.[30] It is an essential component of plant material and present in both coal and biomass.[31] Key Cl induced operational problems include corrosion and ash deposition in the thermochemical facilities. These problems can be very severe and cause unplanned shutdowns and serious damage to various components of boilers if high Cl containing coals, biomass or plastic based fuels are employed. [32] Major environmental impacts created by Cl comprise on particulate matter,[33] chloromethane,[34] dioxin and furan emissions.[35] These environmental problems affect atmosphere, human health as well as flora and fauna.

2.1.1 Operational Challenges

- **Corrosion**

Role of Cl in the corrosion of coal fired boilers was known even in the early 20th century.[36] Since then, significant efforts are made to understand the mechanisms of Cl induced corrosion, slagging and fouling. Cl generally causes corrosion on the furnace walls in the reducing conditions.[37] HCl and Cl_2 in the flue gas can penetrate into the protective coating of tubes and start reacting with Fe to form $FeCl_2$. This $FeCl_2$ further oxidizes to form Fe_3O_4 and Fe_2O_3 releasing Cl_2 for fresh chemical attack. [38, 39] Overall, Cl basically destroys the oxidative protective layers. Cl can also contribute to fireside corrosion by assisting in the formation of KCl which can be deposited. [40] It is noteworthy that Cl_2 is not produced during combustion of coal itself but can form in reducing conditions of boiler.[37] Cl is also known to play a significant role in the corrosion problems of biomass to energy facilities. [41, 42,43] HCl release itself does not play a significant role in corrosion during biomass combustion. However, it assists in the formation of alkali chloride salts which cause severe

corrosion.[32, 44] Detailed mechanism of Cl induced corrosion has been provided by Grabke et al. [45] Briefly, HCl formed during pyrolysis stage gets converted into Cl_2 which reacts with Fe to produce $FeCl_2$. This $FeCl_2$ produced can be converted into Fe_2O_3 or Fe_3O_4. This mechanism has been verified by field testing [46] and establishes the significance of Cl in the corrosion.

- **Fouling**

Ash deposition is considered as one of the important parameter on the applicability on any fuel in energy recovery processes. Ash deposition is known to occur through four possible mechanisms including inertial deposition, thermophoresis, condensation, and chemical reaction.[47] Role of Cl in the propagation of ash depositing is well documented.[48, 49] Alkali metals and Cl can combine to form alkali chlorides which tend to deposit and form a sticky layer on the heat exchanger surfaces.[50, 51] Biomass contains higher amount of Na, K and Cl and lower Sulfur (S) contents. This fuel composition facilitates the formation of ash deposition during combustion and gasification of biomass fuels.

2.1.2 Environmental concerns

- **Particulate Matter Emission**

Cl has been known to contribute to Particulate matter emissions. Recent developments highlighted the significance of Cl as the key contributor in PM_1 emissions.[33, 52] During the pyrolysis stage of combustion, Cl is released into volatiles along with AAEM species. These species become supersaturated in the flue gas. Supersaturation may result in particle formation through homogeneous nucleation or heterogeneous condensation. Once these particles are formed, they collide with each other and adhere. This process leads to the formation of PM_1 particles. [53]

- **Chloromethane Emission**

Chloromethane (CH_3Cl) is known to contribute in stratospheric ozone depletion.[54] Previously, it was believed that CH_3Cl mainly originates from marine sources, however discrepancy in its estimated global sink and sources have led the investigations into terrestrial sources. Biomass is long known for the emissions of CH_3Cl and its mechanism has recently been explained.[34, 55] It is demonstrated that pectin, which is commonly present in plant materials, acts as a methyl donor during low temperature heating of biomass. This methyl combined with Cl^- ions to form CH_3Cl which is released during the early stages of combustion.

- **Dioxins and furan emissions**

Dioxins and furans are produced and emitted during combustion of high Cl containing fuels.[56,57] These emissions are significant in municipal solid waste incineration facilities. However, biomass combustion can also contribute in these emissions. [56] Due to their toxic nature and severe health effects, there are strict limits for dioxins and furan emissions. [57]

2.2 Methods of Cl Determination in Solid Fuels

Quantification of Cl has received a lot of attention by previous researchers due to its significance in coal and biomass thermochemical processes. Accurate quantification of Cl is fundamental requirement for any efforts of addressing its detrimental effects. Therefore, a number of standard methods have been developed for the quantification of Cl as summarized in table 2-1. It is obvious that combustion based method are more commonly employed, as standards, for the determination of Cl in coal. Combustion based methods convert fuel Cl into HCl or salts which can be subsequently recovered. Therefore, complete conversion of Cl into a recoverable form and its capture are important for accurate Cl quantification.

Table 2-1 Standard methods for Cl determination in solid fuels

Fuel	Organization	Method
Coal	ASTM D4208-13	Standard Test Method for Total Cl in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method
Coal	ASTM D6721-01(2006)	Standard Test Method for Determination of Cl in Coal by Oxidative Hydrolysis Microcoulometry
Mineral Fuels	UNE (Spanish Standard) 32024:1995	Solid - Determination of Cl Using Eschka Mixture
Coal and coke	BS 1016-106.6.1:1997	Determination of Cl content Eschka method
Solid mineral fuels	ISO 587:1997	Determination of Cl using Eschka mixture
Coal and coke	AS 1038.8.1-1999 (R2013)	Cl - Eschka method
Coal and coke	AS 1038.8.2-2003 (R2013) :	Cl - High-temperature combustion method
Solid biofuels	DIN EN 15289 (2011-04)	Determination of total content of sulfur and Cl
Solid recovered fuels	DIN EN 15408 (2011-05)	Methods for the determination of sulphur (S), Cl (Cl), fluorine (F) and bromine (Br) content
Refuse-Derived Fuel	ASTM E776-87(2009)	Standard Test Method for Forms of Cl in Refuse-Derived Fuel

However, it has been reported that Cl might be released in forms other than HCl during pyrolysis stage.[27, 34] Moreover, Cl determination methods for biomass and refused derived fuels are contextualized from coal based methods. Applicability of these methods might be limited due to difference in fuel structure, occurrence of Cl in fuel and a wider range of Cl biomass and plastic fuels.

2.3 Occurrence of Cl

2.3.1 Occurrence of Cl in Coal

Occurrence of Cl in coal is a subject of interest since the recognition of its deleterious effects. Presence of Cl in coal has been reported in both organic[31, 58-64] and inorganic[31, 58, 62-64] forms by many researchers since early 20th Century. Even though there have been significant developments in the understanding of the mode of occurrence of Cl in coal, yet the final mode/s of Cl in coal are still debatable.

Organic Cl in coal can be of two types: 1) as the part of organic structure through covalent bond (Cl_{org}) and 2) as Cl^- ions present in the moisture of pores and anchored to the organic structure. The presence of Cl_{org} was demonstrated by indirect methods such as leaching coal with organic solvents[63, 64], pyrolysis,[65, 66] and establishing a negative correlation of Cl with ash and positive correlation with fixed carbon.[31,67] However, no direct evidence has been provided, instead it has been shown by Fyens et al[68] that no covalently bond organo-Cl compounds exist in coal. Idea of the presence of Cl_{org} in coal was originated in 1950s where researches like Gupta, Chakarbati and Edgcombe[69] found that not all the Cl can be extracted by water from coal. Das Gupta and Chakarbati further presented a dedicated method to determine organically associated Cl in the coal.[58] Inability of Cl to be leached by water and acid washing has been considered as the proof of the presence of Cl_{org}. However, this observation alone is not conclusive to demonstrate the presence of Cl_{org} and water insoluble Cl can arise from the inability to water to access Cl^- ions as argued by Huggins et al.[70] Direct evidence of the presence of Cl^- ions in association with moisture anchored to the maceral structure of coal has been provided by different studies using XAFS spectroscopy and Neutron Activation Analysis.[70, 71] Huggins and Huffman presented a novel model on the basis of XAFS spectroscopic observations. It suggests that Cl is present in moisture as Cl^- ions anchored to the positive polar organic groups at maceral moisture interface through an ionic bond. This model explains some of the complications of Cl occurrence.

During the earlier half of 20th century coal researchers believe that Cl is mainly present as alkali or alkaline earth metal salts in coal.[58] Concept that Cl is present as AAEM salts was mainly challenged by the observation of low temperature Cl release during pyrolysis.[65] Pearce demonstrated that Cl is evenly distributed in the coal structure and does not present as NaCl or KCl particle form.[27]

It has also been suggested a part of Cl is present in coal in the form of HCl complexes attached to quaternary ammines. This form of Cl occurrence in coal is supported by the observations that ammonia release with HCl during coal pyrolysis particularly below 450 $^{\circ}$C.[72]

The model presented by Huggins and Huffman can address some of the peculiarities of Cl occurrence. For example, a part of Cl which is water insoluble can be due to the limited access of water to the pores structure thereby presenting water insoluble Cl. Presence of Cl uniformly in coal as observed by Pearce can also be explained.[27] Similarly negative correlation of Cl with Ash and positive correlation with fixed carbon content fits well into the model. This model can also explain the sink float behavior of Cl i.e. the organic affinity of Cl which favors the maceral rich float. Pyrolysis of Illions coal also provides evidence of HCl release with NH_3 species. The results indicated that Cl might be present with Nitrogen species in pore structure of coal.[73] However, possibility of Cl present in other forms cannot be completely eradicated. These possibilities include: presence of AAEM salts after drying if the solutions are saturated, inclusion of Cl as a part of mineral matter, and Cl as an impurity in the mineral matter associated with coal.

2.3.2 Occurrence of Cl in Biomass

Cl is present in plants mostly in water soluble form. [19, 74-76] Plants can uptake Cl form the seeds, soils, water and atmosphere.[77] Cl serves as a micronutrient in the plants and its deficiency could lead to smaller yields and unhealthy growth.[78, 79] Another important role of Cl in the plants is to balance the charge and generally soil has more

Cl than required for plant growth.[37] Once Cl is up taken by the plant it is quite mobile and moves to all parts of the plant. [80] In the case of mallee biomass, quantity of Cl in leaf and bark is more than wood.[19] In biomass, Cl is mainly present as a free ion or loosely bound to exchange sites. However, Cl containing organic compounds like quaternary ammonium chloride may also be present in the plants.[81]

2.4 Cl Release during Pyrolysis

2.4.1 Cl Release during Coal Pyrolysis

Coal pyrolysis is an ancient process and Cl behavior during pyrolysis is well established.[82, 83] Since the contribution of Cl in corrosion of boilers have been realized, efforts are made to understand the release behavior of Cl during pyrolysis process as it is the earlier stage of combustion.[36] Earlier studies on the release of Cl during pyrolysis of British coals include Edgcombe's work on British coals in air atmosphere at 200 °C. Edgcombe discovered that when coal is heated in air more than 50% of Cl is liberated as HCl. However, no Cl is released during heating of coal under Nitrogen atmosphere. [65] This observation however, was made on a relatively low temperature and release of Cl during pyrolysis starts around 200 °C depending upon the mode of occurrence of Cl. On the contrary, Daybell and Gibb showed that Cl is released as HCl at 200 °C on treating British coals under pyrolysis conditions. Particularly, Gibb reported that 97% of Cl is released as HCl during pyrolysis at 258 °C.[72] According to Pearce, the release of Cl as HCl starts from 180 °C for coal when heated in Nitrogen atmosphere. He further made two significant observations. Firstly, that release of Cl during pyrolysis is rapid in the 1st hour and completes after 24 hrs. Secondly, release of Cl depends upon particle size of coal i.e. finer grinding yields more Cl during pyrolysis.[65] Similarly, More than 90% of Cl was released from the fixed bed pyrolysis of Illinois coal as HCl between 300-600 °C.[72] Even though, Pearce also reported the Cl is released with some organic compounds yet, the possibility of HCl reaction with tar species during pyrolysis cannot be eliminated. Most researchers reported that Cl is mainly released in the form of HCl.

Effects of reactor configuration on the Cl release have been studied by Quyn et al on Victorian Brown coal.[84] They demonstrated that volatilization of Cl, as HCl, range from 50-80% from 500-900 °C during fixed bed pyrolysis under slow heating rate. However, during fast heating with volatile char interactions about 75% of Cl was volatilized at 500 °C. With the increase in temperature from 500 – 800 °C, Cl starts to combine with nascent char. With the increase in temperature to 900 °C Cl start to release again up to 50% demonstrating that some of the recombination bonds were not thermally stable in the nascent char.

Efforts have been made to correlate the Cl release with the rank of the coal however, no direct inference was drawn.[85] Three coals containing similar carbon contents demonstrated various Cl release profiles and give four different peaks at 280, 360, 510, and 580 °C for HCl release with only last peak was common in all the three coal samples. Furthermore, no Cl_2 was detected during pyrolysis of any coal sample. This difference in release behaviour could be attributed to the various forms of Cl present in the coals or the re-combination of released HCl with nascent char.[86] Further efforts were made to explain the HCl release peaks by pyrolysing activated carbon with NaCl hydrate, $CaCl_2$ hydrate, and organic hydrochlorides. These model compounds always present HCl peaks below <450 °C. HCl release peaks below 450 °C tend to reduce by water washing of coal. Therefore, Cl which is released at temperatures below 450 °C could be due to presence of organic hydrochlorides, and/ or water soluble Cl^- ions in the moisture of pore structure. However, Cl released above 450 °C could be either by water insoluble forms of Cl originally present in the coal or by inorganic/organic (more likely) Cl species formed by the secondary reactions of HCl in nascent char. [28, 43, 86] Possible reaction sites for HCl in the nascent char include CaO, FeO or activated organic sites which can release HCl on further heating. [28, 87]

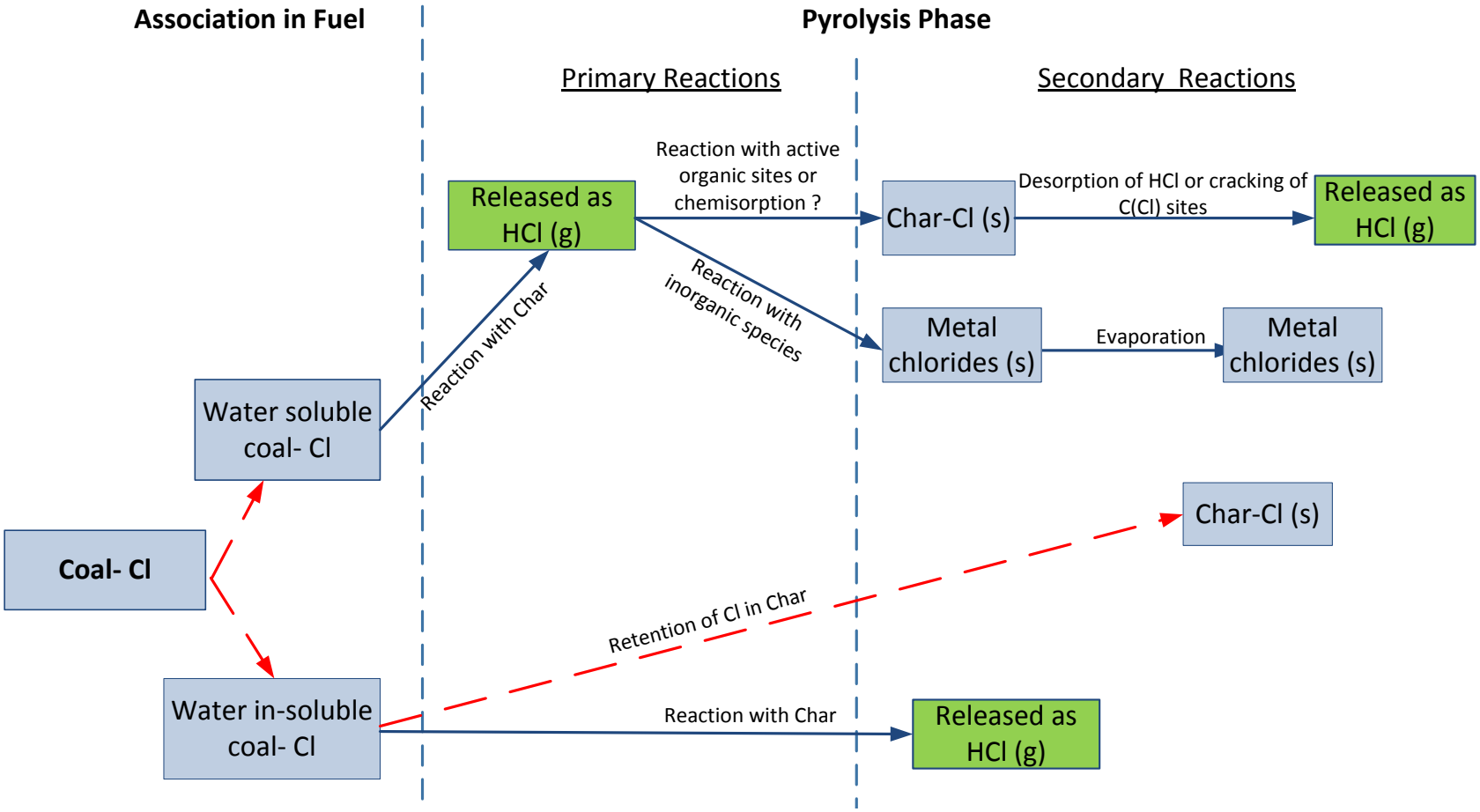

Figure 2-1: Possible reaction pathways and mechanisms during biomass pyrolysis summarised based on literature review findings in section 2.4.1

2.4.2 Cl Release during Biomass Pyrolysis

Cl content of biomass is generally higher than coal.[31, 88] Unlike Cl release during coal pyrolysis that has been studied for a long time, Cl release during biomass pyrolysis is relatively less understood.[29] During pyrolysis of most biomass fuels, Cl release occurs in two steps. First step comprise on the Cl release below 400 °C while the second step includes Cl release above 700 °C. Two-steps Cl release is the trend of most biomass fuels reported in the previous studies[25, 29, 43, 89]; however there are exceptions where nearly all the Cl is release below 500 °C.[90] The extent of low temperature release depends upon the Cl content of the fuels i.e. fuels with low Cl content tend to yield more Cl during low temp pyrolysis.[91 89, 92] Even after the release of Cl at high temperature i.e. 900 °C, 30 – 60% of Cl is retained in char.[29] Complete dechlorination of char has been reported from 1000 °C[93] - 1150 °C.[94]

Low temperature release of Cl is of significant importance due to its operational and environmental implications during biomass pyrolysis. Cl during pyrolysis at low temperature can release in the form of chloromethane (CH_3Cl)[34, 55] and/or HCl. [29, 91, 94] CH_3Cl release is originated by the heating of biomass at low temperatures. Pectin is a ubiquitous component in biomass which acts as a methyl donor. This methyl group combines with Cl to form chloromethane. Low temperature release of Cl is still understudy and different mechanisms have been proposed to explain this phenomenon as summarized in Table 2-2. Björkman et al. suggested that Cl is released by the reaction of KCl and steam in the presence of an acidic oxide. However, heating of KCl with sand does not release any Cl hence indicating that Cl release is not affected by reaction with SiO_2. Zintl et al. provided an ion exchange based mechanism which is further endorsed by various studies.[95,92, 96] High temperature release of Cl is mainly in the form of KCl evaporation.[94, 97] It is also reported that Cl release increase in high heating rate under fluidized bed combustion due to increase tar yield.[95] Based upon the literature review of Cl release studies possible pathways and mechanisms of Cl release are presented in figure 2-2.

Table 2-2: Mechanisms proposed for low temperature Cl release during biomass pyrolysis

Study	Mechanism proposed
Björkman[29]	$2KCl + nSiO_2 + H_2O(g) \rightarrow K_2O(SiO_2)_n + 2HCl(g)$.....(1)
Zintl[96]	$RCOOH(S) + KCl(S) \rightarrow RCOOK(S) + HCl(g)$ .....(2) $RCOOK(S) \rightarrow R + CO_2(g) + K(g)$ .....(3)
Jensen[25]	Cl is released from its binding site and transform into tar phase. Afterwards, it can either release as HCl or react with K and/or basic functionalities.
Hamilton[34]	Low temperature release of Cl can be in the form of CH_3Cl which is formed by heating of Pectin in the presence of Cl^- ions.
Van Lith[90, 92]	Release mechanism of Cl from fibre board is the reaction of metal chlorides with the char during devolatallization. $Char - COOH + MCl(S) \rightarrow Char - COOM + HCl(g)$.....(2)

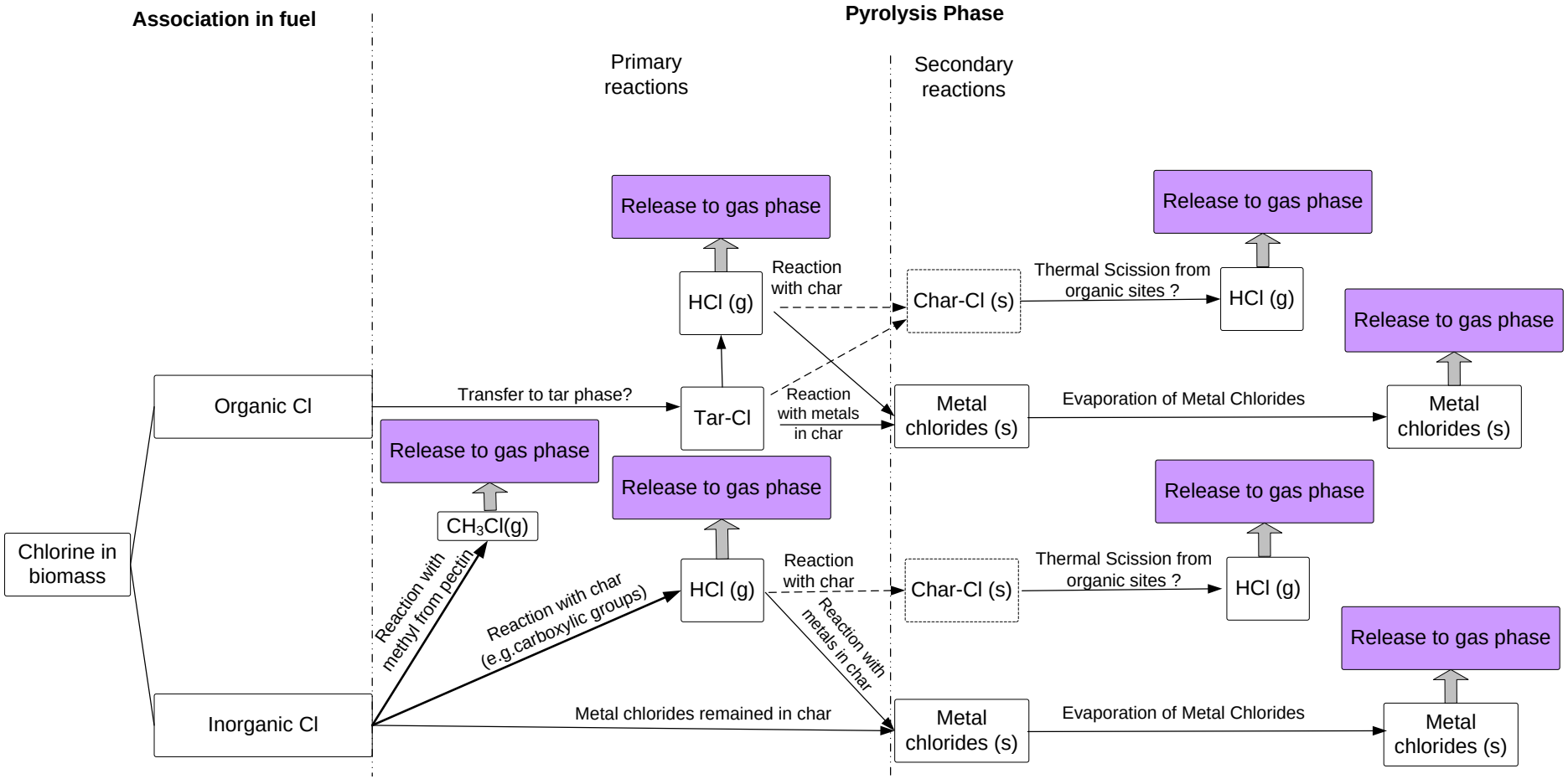

Figure 2-2: Possible reaction pathways and mechanisms during biomass pyrolysis summarized based on literature review findings in section 2.4.2

2.5 Summary of Literature Review and Research Gaps

Based upon the background information and literature review presented above, main conclusions draws are as under.

1. Cl is a key element in the application of biomass in thermochemical facilities from both operational and environmental purposes.

2. Conventional combustion based methods for quantification of Cl may not be able to quantify Cl in all solid fuels.

3. In both coal and biomass, Cl is mainly present as as free ion or loosely bound to exchange sites. However, possibility of other mode of occurrences of Cl cannot be ruled out.

4. Release behaviour of Cl during coal pyrolysis has been extensively studied previously. However, Cl release behaviour during biomass pyrolysis requires further studies.

Conclusion drawn from the literature review of previous studies on the behaviour of Cl during coal and biomass thermochemical conversion imply that following key research gaps require research and development to be addressed.

1. A universal method needs to be developed for the accurate quantification of Cl in all solid fuels.

2. Low temperature Cl release mechanism during biomass pyrolysis needs to be explained.

3. Effect of reactor configuration on the release behaviour of Cl during pyrolysis needs to be studied in detail.

4. Detailed understanding on the transformation of Cl and its interaction with inorganic species during pyrolysis, combustion and gasification still needs to be developed.

5. Strategies to mitigate Cl induced operational and environmental challenges needs to be developed.

2.6 Research Objectives of Present Study

Literature review has identified several research gaps in the research field. However, it is not possible to address all the research gaps during PhD studies over a period of three years. Therefore, this study will focus on following research objectives

1. To develop a universal method for Cl determination in solid fuels aiming to address the limitation of combustion based methods.

2. To explain the Cl release behaviour during pyrolysis of a model compound in order to establish a baseline understanding of Cl release behaviour during biomass pyrolysis.

3. To Study the behaviour and distribution of Cl during biomass pyrolysis under various reactor configurations.

CHAPTER 3 RESEARCH METHODOLOGY AND ANALYTICAL TECHNIQUES

This chapter presents the research methodology and analytical techniques employed to achieve the research objectives mentioned in Chapter 2.

3.1 Methodology

In order to achieve three major objectives outlined in section 2.6, different experimental methodologies were adopted which are briefly described below with the details of sample preparation, experimental rigs and analytical methodologies are given in subsequent sections.

- **Objective 1: Quantification of Cl**

Two methods for Cl quantification i.e. two-step and improved Eschka method were developed in this research project. In two-step method 5 samples were used as standard including cellulose char, 3 NaCl loaded cellulose chars at various loading levels and Polyvinyl chloride (PVC). Standard samples were pyrolysed at 500 $^{\circ}$C with in situ volatile combustion and subsequent capture of HCl in gas bubblers. Char prepared under these experiments were analysed by conventional Eschka method. Two-step method is also applied to determine Cl content of mallee bark, Victorian brown coal and water washed Victorian brown coal. A set of experiments was carried out on Victorian brown coal both with and without volatile combustion.

In improved Eschka combustion method PVC, mallee bark, Victorian brown coal, sub-bituminous coal, and an anthracite coal were used as samples. These samples were subjected to conventional Eschka combustion with flue gas re-combustion. Cl in flue gas was determined by gas bubbler line, while in ash was quantified by ion chromatography (IC). Results obtained by using conventional Eschka method were compared with Two-step method.

- **Objective 2: Cl release behaviour during pyrolysis of a model compound**

In order to study the Cl release behaviour during low temperature pyrolysis a model compound was developed. NaCl was loaded in cellulose through wet impregnation at a loading level of 2.0±0.1 mg Cl/g cellulose. This sample was then pyrolysed with and without volatile combustion in the temperature range of 150 – 400 °C. Chars produced during pyrolysis were water washed to determine water insoluble Cl and Na species.

- **Objective 3: Behaviour and distribution of Cl during biomass pyrolysis under various reactor configurations**

Mallee bark sample is pyrolysed from 400-900 °C with subsequent capture of HCl in the bubbler line under three different reactor configurations including fixed bed, drop-tube/fixed-bed reactor with continuous feeding, and drop-tube/fixed-bed reactor with pulsed feeding. Pyrolysis followed by *in situ* combustion of volatiles in a two-column pyrolysis/combustion reactor was carried out under fixed bed and drop-tube/fixed-bed reactor with continuous feeding configurations.

3.2 Sample Preparation

Basically, 6 samples were used in this research project including: PVC, cellulose, mallee bark, Victorian brown coal, sub-bituminous coal, and anthracite coal. Some samples were derived from these basic samples by using water washing, wet impregnation, and pyrolysis. Details of each sample, its derived samples are given below.

3.2.1 PVC

PVC is used as a standard sample in the development of both two-step and improved Eschka combustion methods (chapter 4 and 5). It is purchased from Sigma-Aldrich (Product No. 81388). The PVC sample was sieved to 75–150 μm for experiments. It has a standard Cl content of 567.3 mg per g PVC (db) and all Cl is organically bound.

3.2.2 Cellulose

Inorganic-free microcrystalline cellulose is purchased from Sigma-Aldrich (Product No. Avicel PH–101, particle size of 30–50 μm) is employed in the development of two-step method and to study the Cl release behaviour during pyrolysis of a model compound (chapter 4 and 6).

In the development of two-step method (Chapter 4) char is prepared from the slow-pyrolysis of cellulose at 310 °C. Cellulose was first washed with Milli-Q water at room temperature to remove water-soluble compounds. The char, referred as "cellulose char" hereafter, is Cl-free. Its derived standard samples were prepared by loading a known amount of NaCl into the cellulose char via wet impregnation. Briefly, a known amount of cellulose char was mixed with a solution of water and a known amount of NaCl in a beaker to prepare char-water slurry. The slurry was then stirred for 24 hours and dried at 35 °C to obtain a NaCl-loaded cellulose char sample. The Cl contents in the three NaCl-loaded cellulose chars are 1.8, 4.6, and 6.6 mg per g of char (db), respectively. In order to study the Cl release behaviour during pyrolysis of a model compound, washed cellulose was loaded with sodium chloride (NaCl) via wet impregnation (as described above) at a chlorine (Cl) loading level of 2.0±0.1 mg Cl/g cellulose, on dry basis.

3.2.3 Mallee bark

Mallee bark is used in development of two Cl quantification methods and to study the effects of reactor configuration on Cl release during pyrolysis (Chapter 4, 5, and 7). The bark component was separated from a batch of green mallee trees (*Eucalyptus polybractea*) harvested from Narrogin, Western Australia, Australia. The bark sample was then further processed by cutting and sieving to prepare a size fraction of 75–150 μm after drying at 40 °C for 24 h. The resulting sample is hereafter referred to as "raw biomass".

3.2.4 Victorian brown coal

Victorian brown coal is used in development of two Cl quantification methods (Chapter 4, and 5). Victorian brown coal samples were air-dried, ground, and sieved to a size fraction of 75–150 μm. In two step method study (chapter 4) Victorian brown coal sample was also washed using Milli-Q water for 24 h (at a solid to liquid ratio of ~4 g/L), yielding a water-washed brown coal sample that contains water-insoluble chlorine only. The washed coal was sieved again to 75–150 μm after air drying at 35 °C.

3.2.5 Sub-bituminous coal

The sub-bituminous coal was purchased from Alpha Resources (AR-2780). It was sieved to 75–150 μm, air-dried at 40 °C, sealed in plastic bags, and stored in freezer at -4 °C prior to experiments.

3.2.6 Anthracite coal

Anthracite coal was sieved to 75–150 μm , air-dried at 40 °C, sealed in plastic bags, and stored in freezer at -4 °C prior to experiments.

3.3 Experimental Rigs

3.3.1 Experimental rig used in two-step method

This experimental rig was used to conduct experiments for Two-step method development (chapter 4). A two-stage pyrolysis/combustion quartz reactor (see Figure 3-1) was employed for the production of Cl-containing volatiles and it's in situ combustion. The reactor consists of two zones, i.e., a fixed-bed pyrolysis zone and a tubular combustion zone. Temperatures of the two zones were controlled individually by two independent electrically heated furnaces that were stacked. There are four steps for an experiment. First, the bottom furnace used for heating the combustion zone was preheated to 950 °C. Second, ~1 g of sample was loaded into the pyrolysis zone of the two-stage reactor. Ultra High Purity (UHP) argon (flow rate: 2 L/min) was introduced into the pyrolysis zone. Two streams of oxygen including 0.4 L/min of primary oxygen and 0.4 L/min of secondary oxygen were introduced

into the combustion zone from ports above and below a gas distributor (see Figure 3-1), respectively. Third, once the combustion furnace reached 950 °C, the two-stage reactor was inserted into the two stacked furnaces from the top furnace. A heat insulator was installed between the pyrolysis zone and the combustion zone of the two-stage reactor to minimize thermal radiation from the bottom furnace. The outlet of the two-stage reactor was then connected to bubblers that were loaded with 0.1 M NaOH solution. Fourth and last, the top furnace (hence the pyrolysis zone of the two-stage reactor) was then heated from room temperature to a desired pyrolysis temperature (200–500 °C) at a slow heating rate of 10 °C/min, with a further holding time of 10 min at the pyrolysis temperature. Therefore, during the process of fuel pyrolysis in the pyrolysis zone, once produced, the Cl-containing volatiles were immediately burnt in situ in the combustion zone. The in situ combustion converted Cl in volatiles to ionic chloride (most likely as HCl) in flue gas, which was then captured by the NaOH solution.

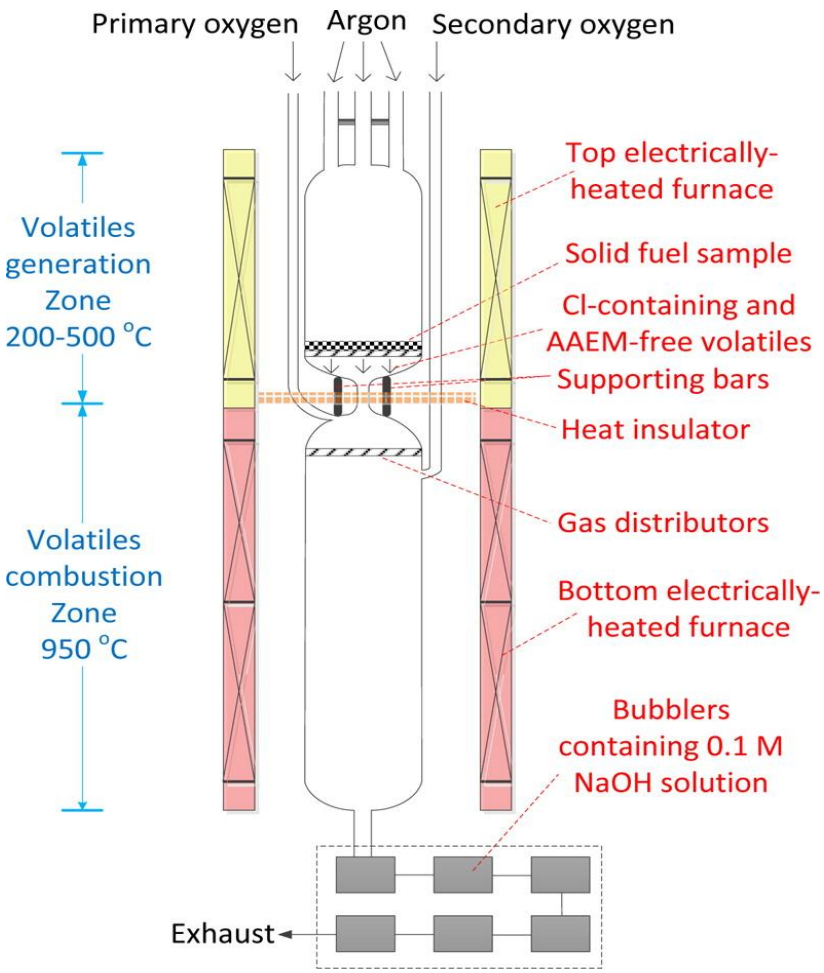

Figure 3-1: Schematic diagram of a two-stage pyrolysis/combustion reactor system.

3.3.2 Experimental Rig Used in Improved Eschka Combustion Method

Figure 3-2 presents the schematic diagram of the experimental setup employed by the improved Eschka method (Chapter 5). It consists of an Eschka reactor required for the conventional Eschka combustion process and an additional combustion reactor for flue gas re-combustion, which is connected to the Eschka reactor via a quartz tube. During an experiment, ~150 mg fuel sample was mixed with ~300 mg of Eschka flux (a mixture of sodium carbonate and magnesium oxide, purchased from Sigma Aldrich, with a product number of 00166) in a platinum (Pt) boat, which was further covered with ~200 mg of Eschka mixture. The flue gas re-combustion reactor was preheated to 950 °C and the quartz connection tube was preheated and maintained at 675 °C. The sample-loaded Pt boat was then placed in the Eschka

reactor, which was heated to 675 °C (heating rate: 10 °C/min, holding time: 2 h; air flow rate: 2 L/min) in accordance with the Eschka method.[98] The flue gas was continuously swept out the Eschka reactor and burned in the combustion reactor in the presence of two streams of oxygen, i.e., primary oxygen (flow rate: 0.4 L/min) and secondary oxygen (flow rate: 0.4 L/min). The flue gas re-combustion process converted the escaped Cl into HCl (g), which was subsequently captured by 0.1 M NaOH solution (in form of chlorides) through gas bubblers.

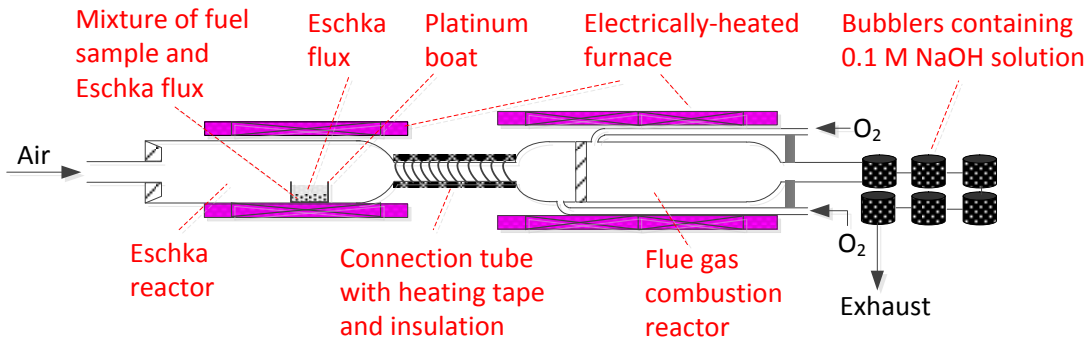

Figure 3-2. Schematic diagram of the experimental setup for the improved Eschka method.

3.3.3 Experimental Rig to Study Cl Release Behaviour during Pyrolysis of a Model Compound

A two-column pyrolysis/combustion quartz reactor (see Fig. 3-3 a) was employed for the slow pyrolysis of the NaCl-loaded cellulose and quantification of Cl released into volatiles via *in situ* combustion (see chapter 6). The reactor consists of a fixed-bed pyrolysis column and a tubular combustion column. The temperatures of both columns were individually controlled by two independent electrically-heated furnaces. The two columns were connected by a quartz tube that was preheated to the pyrolysis temperature via heating tape in order to avoid volatiles condensation. During an experiment, the combustion column was first heated to 950 °C before starting pyrolysis experiment. Two streams of oxygen (O_2, flow rate: 0.4 L/min each) were introduced to the combustion column. About ~0.6 g NaCl-loaded cellulose was loaded into a Platinum (Pt) boat, which was then placed into the pyrolysis column. The pyrolysis of the NaCl-loaded cellulose was then carried out at a temperature ranging from 150 to 400 °C, a heating rate of ~10 °C/min and a holding time of 30

mins. Ultra High Purity (UHP) argon (Ar, flow rate: 2 L/min) was used as carrier gas. The outlet of the combustion column was connected to six bubblers containing 0.1 M sodium hydroxide (NaOH) solution. For quantifying the total Cl in volatiles, the Cl-containing volatiles produced from the slow pyrolysis of the NaCl-loaded cellulose were immediately burnt in the combustion column to convert the Cl in the volatiles into HCl (g) in flue gas, which was then captured by the NaOH solution. For quantifying HCl (g) in volatiles, the Cl-containing volatiles produced from the slow pyrolysis of the NaCl-loaded cellulose were directly introduced to the NaOH solution without combustion (see Fig. 3-3 b).

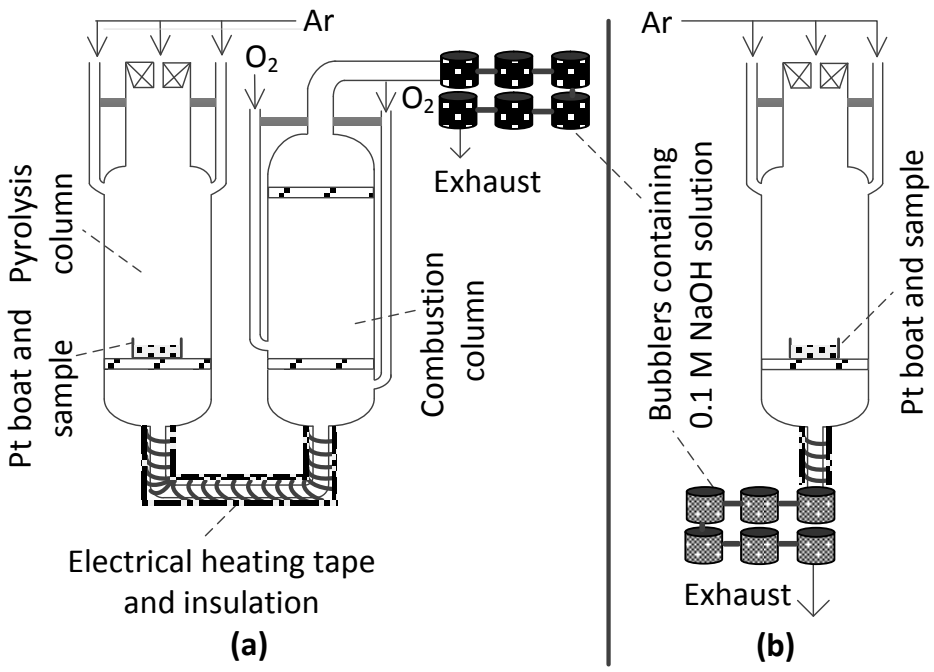

Figure 3-3. Schematic diagram of the experimental system used for the slow pyrolysis of the NaCl-loaded cellulose (a) with and (b) without volatiles combustion

.3.3.4 Experimental Rig to Study Cl Release during Mallee Bark Pyrolysis under Various Reactor Configurations

Three types (I, II, and III) of pyrolysis experiments were carried out in order to study Cl release during mallee bark pyrolysis (See chapter 7), using argon [ultrahigh purity (UHP)] as carrier gas. Type I experiments were conducted in a fixed-bed pyrolysis

reactor system (see Figure 3-3a). Briefly, the reactor was preloaded with ~ 1.0 g of raw biomass sample. The reactor was then heated to a desired pyrolysis temperature at ~10 K min^{-1}, with a further holding of 10 min. The reactor temperature was controlled via a controller with an accuracy of well below 0.5% of the setting temperature. Type II experiments used a drop-tube/fixed-bed reactor (estimated heating rate of ~1000 K s^{-1}) equipped with a continuous feeder (see Figure 3-3 b). A total of ~1.0 g of raw biomass sample was continuously fed into the reactor at a feeding rate of ~100 mg min^{-1}. Once the biomass particles were injected into the hot reactor, rapid pyrolysis took place, producing char particles that remained on the reactor frit, while the volatiles were swept through the char bed. A unique feature of this continuous feeding drop-tube/fixed-bed reactor is that volatiles continuously contact with nascent char particles, resulting in extensive so-called "volatile–char interactions".[99] Type III experiments used the same drop-tube/fixed-bed reactor system but equipped with a pulsed feeder (see Figure 3-3c). Briefly, ~ 0.1 g of raw biomass sample was fed into the reactor in one shot. In both type II and III experiments, the reactor was further held for 10 min in the furnace after the feeding was completed.

All pyrolysis experiments were carried out between 400 and 900 °C, and the gas residence time was kept as ~1.5 s via adjusting the flow rate of carrier gas from 1.5 to 2.6 L min^{-1}. Once a pyrolysis experiment was completed, the reactor was lifted out of the furnace and cooled naturally with argon continuously passing through the reactor. Hereafter in chapter 7, these types of experiments are referred to as "fixed-bed (FB) configuration", "continuous feeding drop-tube/fixed-bed (CFDT/FB) configuration", and "pulsed feeding drop-tube/fixed-bed (PFDT/FB) configuration", respectively. Subsequently, char samples produced from the three types of configurations at 400–900 °C are denoted as "FB-char-XXX", "CFDT/FB-char-XXX", and "PFDT/FB-char-XXX", where "XXX" stands for the pyrolysis temperature. In each pyrolysis experiment, the Cl-containing volatiles (including tar and non-condensable gas) were passed through six bubblers with each

containing ~ 150 g of 0.1 M sodium hydroxide (NaOH) solution to ensure complete capture of Cl in the gas phase. The bubblers were immersed in an ice bath to facilitate the absorption of Cl by the 0.1 M NaOH solution. Typically, tars in the pyrolysis gas were also condensed in the bubblers. Therefore, Cl captured in the solutions is in ionic form, i.e., water-soluble chloride (Cl^-). After each experiment, Cl^- contained in the solutions was quantified.

- ***In Situ* Combustion of Volatiles Generated from Biomass Pyrolysis**

Besides water-soluble Cl (i.e., Cl^- or gas Cl), there may also be water-insoluble Cl (i.e., tar Cl) present in the volatiles collected at the exits of the reactor systems after pyrolysis. To quantify the total Cl in the volatiles, another type of experiment (type IV) was also carried out using a two-column pyrolysis/combustion reactor system (see Figure 3-3 d). Fundamentally, the two-column reactor system consists of a pyrolysis reactor and a combustion reactor in two stages. The pyrolysis reactor can be operated in each of the three types described in the previous section (type I, fixed-bed reactor; type II, drop-tube/fixed-bed reactor with continuous feeding; or type III, drop-tube/fixed-bed reactor with pulsed feeding). In the pyrolysis reactor, biomass pyrolysis took place, generating volatiles that were then combusted *in situ* in the combustion reactor. The *in situ* combustion converts all Cl in the volatiles into ionic form, which can be captured by 0.1 M NaOH solution, enabling the quantification of total Cl in the volatiles. In this study, the pyrolysis reactor was operated at different temperatures (400–900 °C) for type I and II experiments. The combustion reactor was operated at 950 °C. Two streams of oxygen was supplied to the combustion reactor, including primary oxygen (0.4 L min^{-1}) introduced below the bottom quartz frit and a stream of secondary oxygen (0.4 L min^{-1}) above the frit to achieve complete combustion. The flue gas after combustion was then introduced into the bubblers, which were loaded with 0.1 M NaOH solution, for Cl collection and quantification.

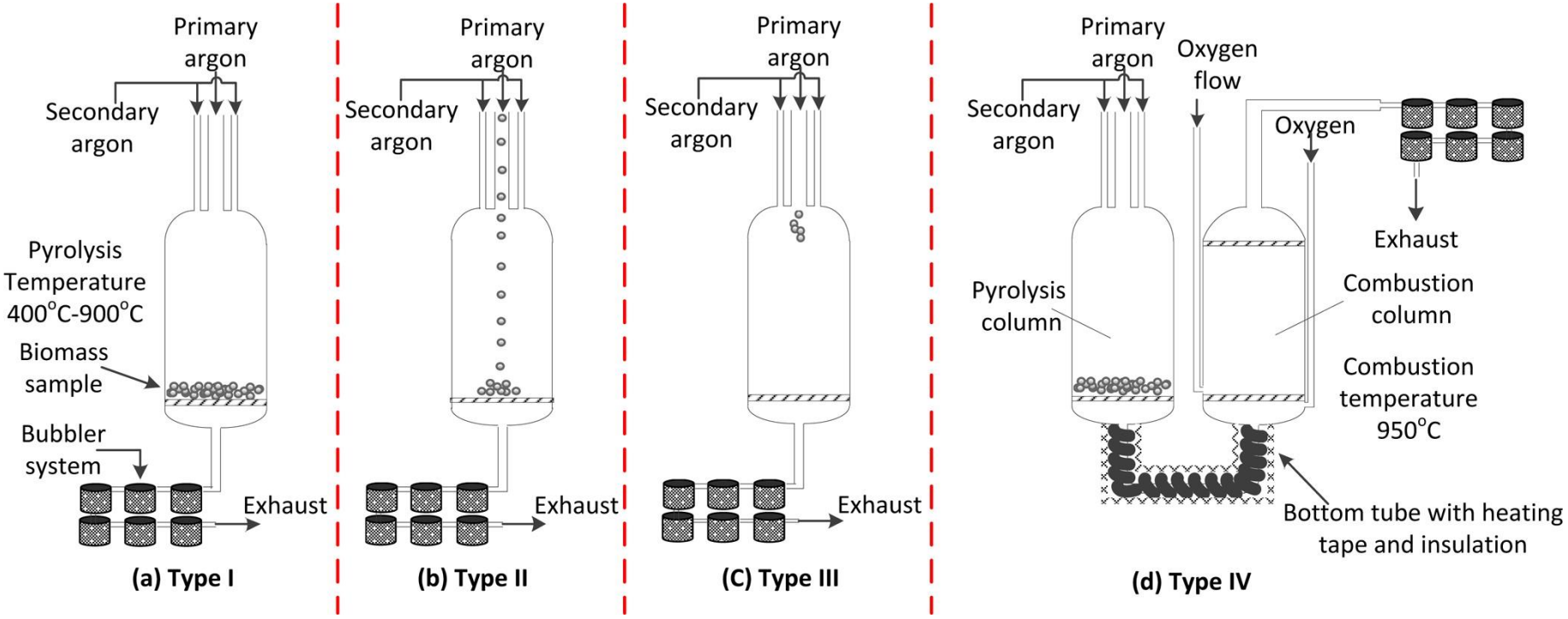

Figure 3-4. Schematic diagrams of four types of experiments carried out in this study: (a) type I, pyrolysis in a fixed-bed reactor; (b) type II, pyrolysis in a drop-tube/fixed-bed reactor with continuous feeding; (c) type III, pyrolysis in a drop-tube/fixed-bed reactor with pulsed feeding; and (d) type IV, pyrolysis followed by *in situ* combustion of volatiles in a two-column pyrolysis/combustion reactor.

3.4 Instruments and Analytical Techniques

3.4.1 Proximate, Analysis and Determination of Ignition Temperatures

Proximate analysis of samples used in chapter 4, 5 and 7 was determined by a METTLER thermogravimetric analyzer (TGA) based on American Society for Testing and Materials (ASTM) international standard ASTME870-82[100] and ASTMD7582-10,[101] the temperature program of TGA is shown in Figure 3-5. Briefly, ~10 mg of fuel sample was loaded into the TGA sample crucible, purged with Ar for 15 min and then heated to 110 °C followed by holding at this temperature for 20 minutes until no further weight loss was observed. The total weight loss was recorded as moisture content of the sample. The sample was then further heated to 950 °C at a heating rate of 50 K min^{-1} in Ar and held at the temperature for 20 min, followed by decreasing the temperature to 600 and 750 ^{o}C for biomass and coal, respectively. The weight loss was recorded as volatile matter and the remaining material as char. The char residue was then exposed to air to be oxidized for 30 min until no weight loss was observed. The weight of the residual ash in the sample crucible is used to calculate the ash content of the fuel, while the difference between the weights of the char and residue ash is calculated as the fixed carbon content of the fuels.

Ignition temperature of various samples was determined by following a procedure described by Wang et al. (chapters 4 and 5).[102] Briefly, to determine the ignition temperature, a TG and DTG curve is obtained for each sample. Two points on the TG curve are identified i.e. one point at which a vertical line from the sharp DTG peak crosses the TG curve. The other point is at which volatilization starts to appear. Tangents to the TG curve and another horizontal tangent are drawn. The point at which these lines cross is known as ignition temperature.

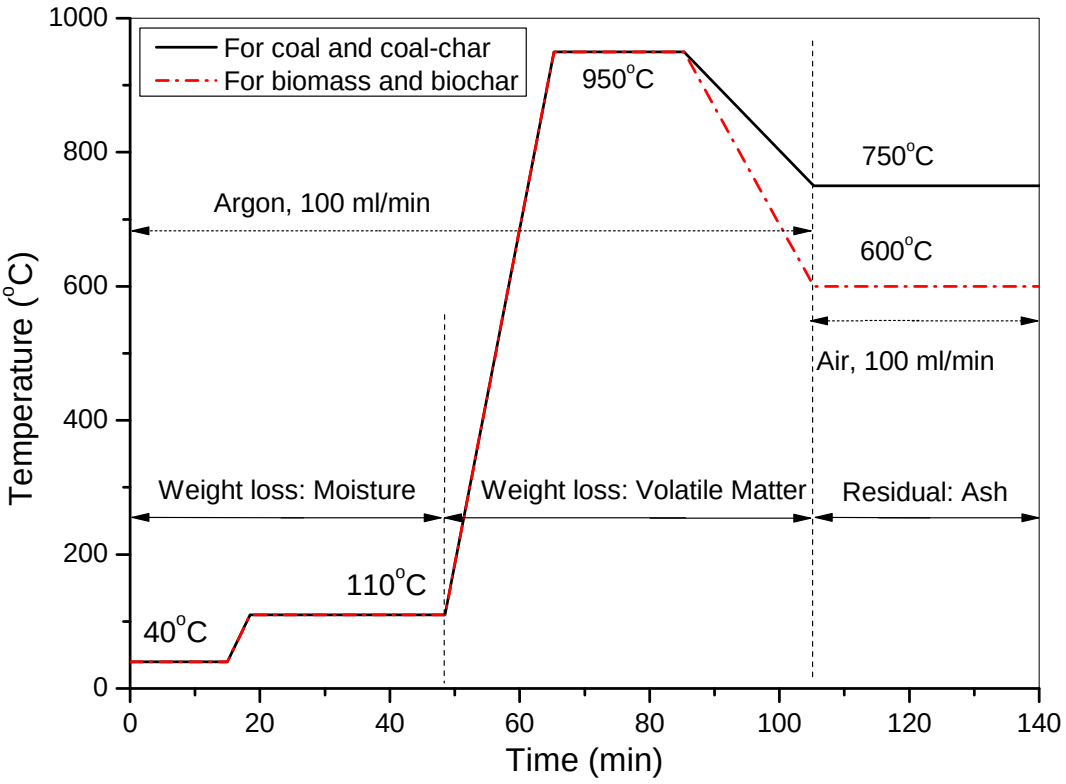

Figure 3-5: Temperature program of TGA for proximate analysis

3.4.2 Ultimate Analysis

Ultimate analysis of these fuels was determined via a series of analytical techniques, total carbon, hydrogen and nitrogen contents were determined using a LECO Truspec Analyser according to Australian standard AS1038.6.4,[103] while the total sulfur were determined by following combustion of the samples under "Eschka" mixture and acid digestion, based on Australian standard AS1038.6.3.1.[104] Chlorine contents of all the samples were determined by Improve Eschka combustion method (See chapter 5). The oxygen contents were determined by the difference from the C, H, N, S and Cl contents of the samples, on a dry-ash-free (daf) basis.

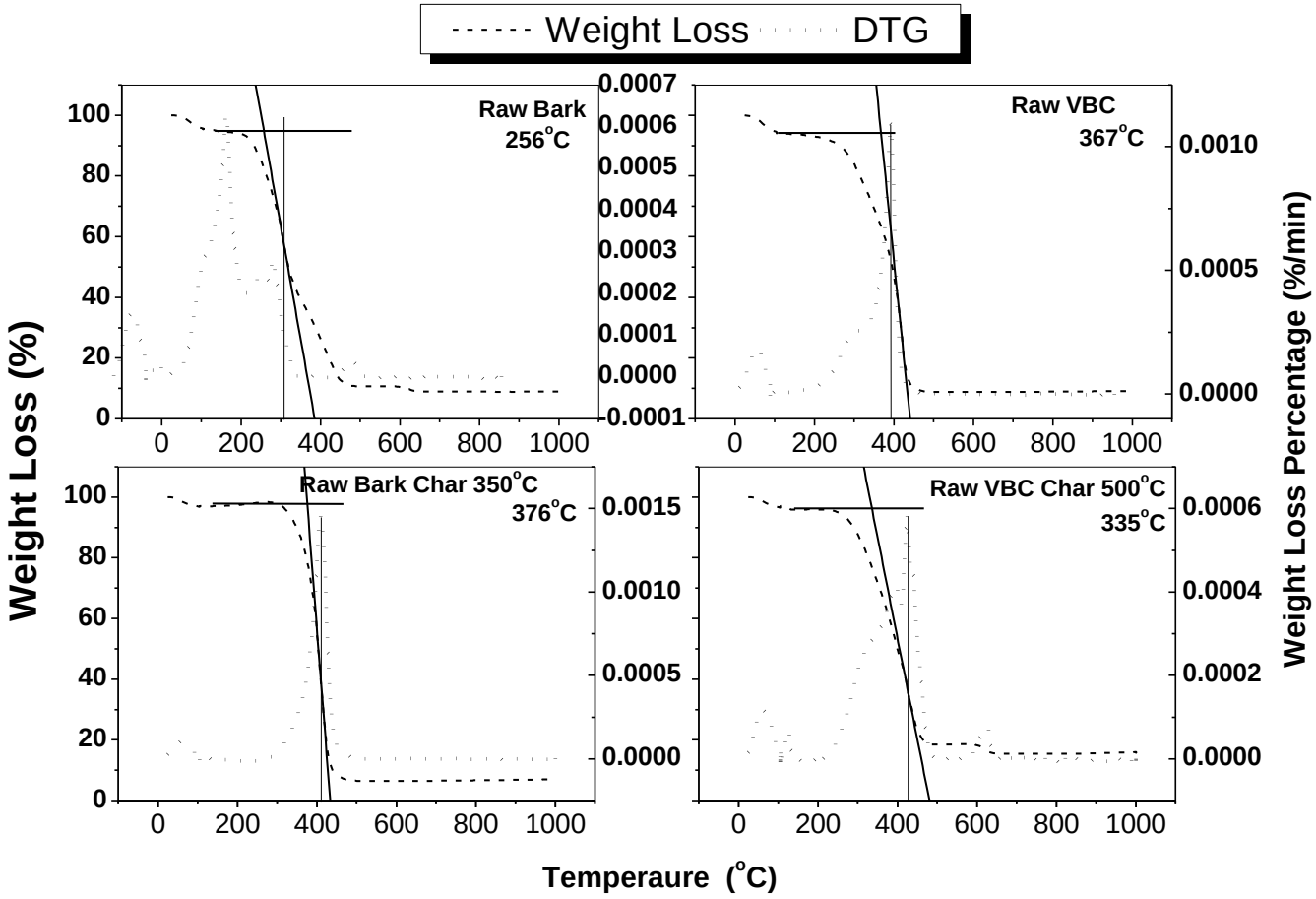

Figure 3-6: Ignition temperature determination procedure of selected samples.

3.4.3 Quantification of Cl in Solution

Cl in the solution was mainly of two types: first is the Cl absorbed in the NaOH solution of the bubbler line (chapter 4-7) and second is Cl extracted by water washing from various samples as presented in chapter 4, 6 and 7.

To quantify the water-soluble Cl content in a biomass or char sample, continuous leaching of the sample using deionized water was carried out using a semi-continuous leaching apparatus. Briefly, 100 mg of raw biomass was leached in the leaching apparatus for 4 h by a continuous flow of deionized water at 100 mL/min, delivered by a high-performance liquid chromatography (HPLC) pump. The leachate was swept out of the reactor, and the biomass sample remained on the frit (Chapters 4 and7). The water-soluble Cl in the NaCl-loaded cellulose and its derived solid residue were also quantified via washing the samples using Milli-Q water under batch leaching conditions for 24 h at a solid to liquid ratio of ~4 gram/L (Chapter 6).

Cl in the leachates was quantified using ion chromatography (IC; model Dionex ICS-1100) with an IonPac AS22 fast analytical column (4 × 150 mm) and 2.25 mM $NaCO_3$/0.7 mM $NaHCO_3$ solution as an eluent. Cl absorbed in the 0.1 M NaOH solution from each pyrolysis experiment was also quantified using the same IC.

3.4.4 AAEM Analysis

AAEM contents of various samples were determined in chapter 3, 6 and 7 using acid digestion procedure. [105] About 20~30mg of fuel sample was put in a Pt crucible, than it was ashed in air following a specially designed heating program to ensure no loss of these species during ashing. The ash sample together with the Pt crucible was then put in a Teflon vial for acid digestion with a mixture of HNO_3:HF (1:1) solution at 120 °C for 12h. After the evaporation of excessive acids on a hot plate, the digested ash was dissolved in 20mM methanesulfonic acid (MSA) solution. The AAEM species in the solution was quantified using a Dionex ICS-3000 ion chromatography

with a CS12A column and 20mM MSA solution as eluent.

3.4.5 SEM Analysis

The raw biomass and selected chars were also characterized using scanning electron microscopy (model: Zeiss EVO 40XVP) equipped with an energy-dispersive X-ray spectrometer (SEM–EDS).

3.5 Summary

Overall, two novel Cl quantification methods were developed in this project by using 6 basic fuel samples and their derived fuels. Two-step method uses pyrolysis with in situ volatile combustion whereas improved Eschka combustion method employ flue gas re-combustion. Release of Cl from NaCl loaded cellulose pyrolysis was conducted with volatile combustion. Cl release during pyrolysis of mallee bark is carried out under fixed bed and drop tube/fixed bed reactor configurations.

CHAPTER 4 A TWO-STEP METHOD FOR THE QUANTIFICATION OF CL IN LOW-RANK SOLID FUELS

4.1 Introduction

Cl is commonly present in low-rank solid fuels such as brown coal (or lignite)[44, 67] and biomass.[19] During combustion or gasification, Cl is responsible for various operating problems such as ash deposition,[106, 107] corrosion,[42, 108] particulate matter emission,[33, 52, 105] and other ash-related issues.[109, 110] Understanding its transformation behavior is important and requires accurate quantification of Cl contents in these fuels.

A number of methods are available for determining Cl contents in solid fuels.[19, 70, 111-122] These methods can be briefly classified into three categories, i.e., combustion-based, hydrolysis-based, and extraction-based methods, as summarized in Table 4-1. The combustion-based methods, including bomb combustion, [90, 123, 124] direct combustion, [89, 125] and Eschka method,[98, 112, 126] were extensively employed in some previous publications. Principally, all these combustion-based methods convert fuel Cl into chlorides that are either released as gaseous HCl or retained in ash as chloride salts, followed by subsequent capture and quantification of the converted chlorides. Thus, the complete conversion of fuel Cl, the exhaustive capture/recovery of the converted chlorides, and their accurate quantification are equally important, in order to obtain credible Cl content in solid fuels.

However, it was reported previously that the combustion-based methods may not be able to meet such essential requirements. For instance, the bomb combustion method might encounter incomplete combustion and thereby fail to convert all fuel Cl into chlorides.[127]

Table 4-1. Methods of Cl quantification in solid fuels

No.	Method	Cl Species	Instrument	Temperature	Absorption	Cl Detection Technique
Combustion-based methods						
1	Eschka method (AS 1038.8.1—1999[128], ISO-587[112])	Total Cl	Muffle furnace	675 ^{o}C[112]	Diluted nitric acid	Modified Volhard method,[128] Mohr titration or Potentiometric titration[112]
2	Direct combustion (AS 1038.8.2)[113]	Total Cl	Tube furnace	1350 ^{o}C,[113] 900 ^{o}C[111]	Hydrogen peroxide solution	Titration,[113] Ion chromatography[111]
3	Oxygen bomb combustion (I.S. EN 15289:2011,[114] I.S. EN 15408,[115] D4208 − 13,[116] D E776 − 87 Reapproved 2009)	Total Cl	Oxygen bomb	-	Water/ alkaline solution, carbonate or bicarbonate solutions or H_2O_2, [114]water or 0.2 M KOH,[115] 2% Na_2CO_3[116]	Ion chromatography / Inductively coupled plasma,[114] Ion chromatography,[115] Ion-selective electrode[116]
4	Microwave-induced combustion technique[121]	Total Cl	Multiwave 3000 microwave sample preparation system	1400 ^{o}C	water or $(NH_4)_2CO_3$ Solution	Ion chromatography
5	Elemental analyzer[127]	Total Cl	Analytik Jena multi® EA 2000	700, 850 or 1000 ^{o}C		Coulometric detector for gas Cl, Ion chromatography for Cl in ash

6	Schöniger flask combustion (EN 14582: 2007) [127]	Total Cl	Schöniger flask		Mixed solution of Na_2CO_3, $NaHCO_3$, and H_2O_2.	Ion chromatography
7	Sintering with inductively coupled plasma-sector field mass spectrometry (ICP-SFMS)[120]	Total Cl	Heraeus KM 170 furnace	560 ^oC (Sintering temperature)	Water leaching with cation- exchange clean-up, microwave-assisted digestion	Inductively coupled plasma-sector field mass spectrometry
Hydrolysis						
8	Oxidative hydrolysis microcoulometery (ASTM D6721 − 01 Reapproved 2006)[117]	Total Cl	Hydrolysis furnace	900 ^oC	Titration cell	Microcoulometery
Extraction method						
9	Modified Kjeldahl method[69]	Total Cl				Gravimetric determination
10	Extraction with solution of 0.1 M $KN0_3$ in dimethyl sulphoxide[119]	Inorganic Cl			Dimethyl sulphoxide	Ion chromatography and titrimetry
11	Water washing[129]	Inorganic Cl				Volhard method

The direct combustion method faces the challenge of the presence of alkali chlorides (e.g., NaCl and/or KCl) vapors in flue gas because these vapors may condense on and/or react with reactor surface and thereby cause Cl loss. [111] The Eschka method relies on the capture of released Cl, in form of HCl (g) using Eschka flux (sodium carbonate and magnesium oxide) during combustion.[98] However, if Cl is released in forms other than HCl (g) during the early stage of combustion (i.e., pyrolysis), it is questionable whether the Eschka mixture can still effectively trap the released Cl.[36]

The quantification of Cl in low-rank solid fuels such as biomass and brown coal using combustion-based methods (e.g., the direct combustion method and the Eschka method) would be more challenging because of their unique fuel properties. On one hand, these low-rank fuels are generally rich in alkali metals (Na and/or K) that are easily volatilized into gas phase during combustion. [130] On the other hand, Cl in these fuels can be released into volatiles, in forms other than HCl (g), during pyrolysis at relatively low temperatures (e.g., 400 °C). Indeed, in chapter 7 it has clearly demonstrated that, during the slow-heating-rate pyrolysis of mallee bark at 400 °C, majority (~77%) of Cl is released associated with tar.

This chapter aims to develop a method for the quantification of total Cl in low-rank solid fuels. The method has two steps, taking advantage of slow-heating-rate pyrolysis as a mean to separate total Cl into Cl released in volatiles and that retained in char. The Cl in the volatiles produced from pyrolysis was quantified via in situ combustion and subsequent capture in 0.1 M sodium hydroxide (NaOH) solution. The Cl retained in the char was then determined using the Eschka method. The total Cl in a fuel was then quantified as a sum of the Cl in volatiles and that in char. Various low pyrolysis temperatures (200–500 °C) and several low-rank solid fuels (i.e., a mallee bark, a brown coal, and a water-washed brown coal) were considered. The two-step method has two key innovations. One is that the volatiles produced from pyrolysis at low temperatures (≤500 °C) at a slow heating rate is free of AAEM, (see chapter 7) minimizing Cl loss during in situ volatiles combustion. The other is

that, after pyrolysis, the Cl in char is stabilized and unlikely to be released during the early stage of the Eschka combustion. The Cl in char can thus be effectively captured using the Eschka method.

Table 4-2. Properties of low-rank solid fuels studied

Samples	Mallee bark	Victorian brown coal	Water-washed Victorian brown coal
Proximate analysis			
Moisture, wt% ad[a]	5.7	5.2	4.4
VM[b], wt% db[c]	77.3	49.7	52.5
FC[d], wt% db[c]	18.0	49.4	46.8
Ash, wt% db[c]	4.7	0.9	0.7
Ultimate analysis (wt%, daf[e])			
C	48.92	68.62	68.28
H	4.97	4.84	5.04
N	0.23	0.67	0.61
S	0.03	0.27	0.28
Cl[f]	0.42	0.11	0.06
O[g]	45.43	25.49	25.73
Contents of AAEM species (wt%, db[c])			
Na	0.1364	0.0943	0.0112
K	0.2589	0.0018	0.0010
Mg	0.2062	0.0655	0.0643
Ca	1.3677	0.0829	0.0857

[a] Air-dried basis; [b] Volatile matter; [c] Dry basis; [d] Fixed carbon; [e] Dry and ash-free basis; [f] Quantified based on the *two-step volatiles-in-situ-combustion/char-Eschka* method, with pyrolysis temperature of 500 ^{o}C; [g] By difference.

4.2 Design and validation of a two-step method for quantifying cl in low-rank fuels

Figure 4-1 depicts an overview of the two-step method for quantifying Cl in low-rank fuels. Using the two-stage reactor (see Figure 3-1), total Cl in a fuel sample is separated into Cl released in volatiles and that retained in char via slow pyrolysis at pyrolysis temperatures between 200 and 500 °C. The Cl in volatiles is

then in situ combusted, captured in 0.1 M NaOH solution, and quantified by IC (see Section 3.3.1). In the second step, the Cl retained in char is determined by the Eschka method.[98] The total Cl (Cltotal, mg/g fuel, db) can thus be calculated as follows:

$$Cl_{total} = Cl_{volatiles} + Cl_{char} \times \frac{Y_{char}}{100} \quad \text{.....1}$$

where Cl $_{volatiles}$ (mg/g fuel, db) is the Cl recovered in volatiles. Cl $_{char}$ (mg/g char, db) is the Cl content in char and Y $_{char}$ (wt%, db) is the char yield from slow pyrolysis.. Properties of low-rank solid fuels studied are given in table 4-2.

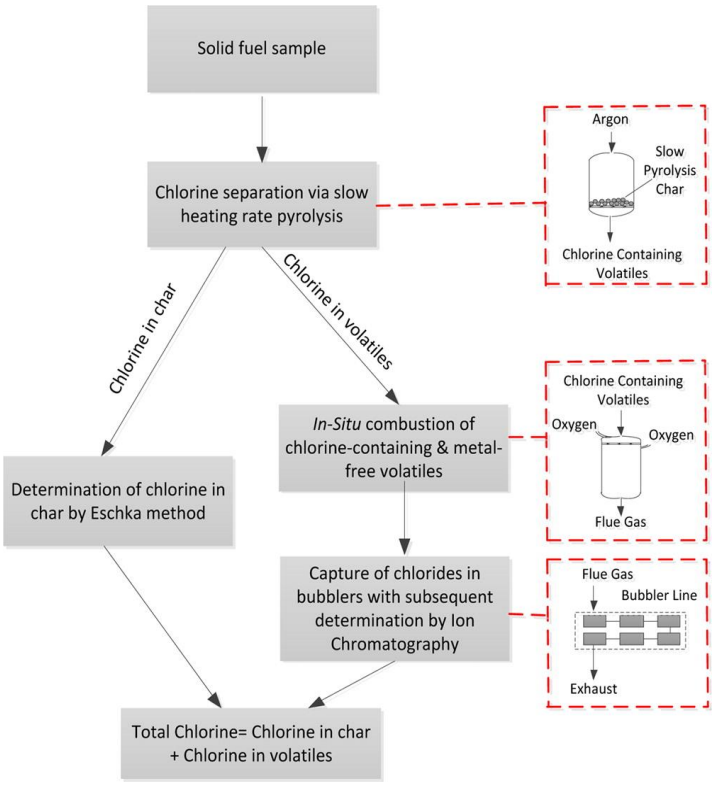

Figure 4-1: Design of the proposed two-step method for quantifying Cl in low-rank fuels.

Slow pyrolysis was chosen to separate fuel Cl for three reasons. First, during slow pyrolysis, volatiles are released slowly and progressively. This nature lowers the concentration of combustible matter in volatiles and in turn eases its complete combustion. Second, during slow pyrolysis, volatiles produced can be swept away immediately, minimizing recombination of Cl into char. Third, slow pyrolysis

produces volatiles free of AAEM species. (see chapter 7) At 200–500 °C, the yields of char and volatiles from the slow pyrolysis of the bark, brown coal, and water-washed brown coal samples are shown in Figure 4-2. Under such slow heating conditions, 100% of AAEM species are retained in char during the pyrolysis of the bark, brown coal and water-washed brown coal samples, as shown in Figure 4-3.

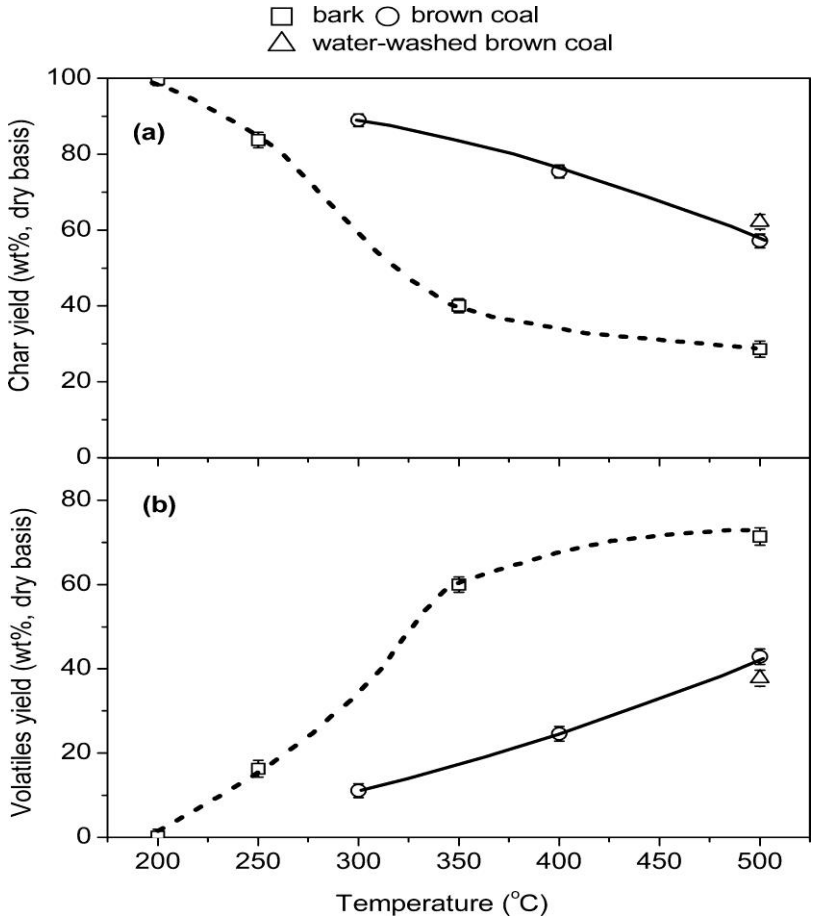

Figure 4-2: Yields of (a) char and (b) volatiles from the slow pyrolysis of the bark, brown coal, and water-washed brown coal samples. 11

The production of volatiles free of AAEM species is particularly important because AAEM species (especially alkali metals) in volatiles would react with Cl during combustion and the alkali chlorides formed may deposit on and/or react with quartz reactor. In fact, during direct combustion of the bark and the brown coal in a drop-tube quartz reactor at 950 °C, only 1.1 and 0.2 mg of Cl per gram of fuel (db) were recovered from flue gas. Such recovery rates are significantly lower than those (~ 4.0 and ~1.1, respectively) from the in situ combustion of AAEM-free volatiles

generated from the slow pyrolysis of these fuels at 500 °C (see subsequent discussion in Section 4.3).

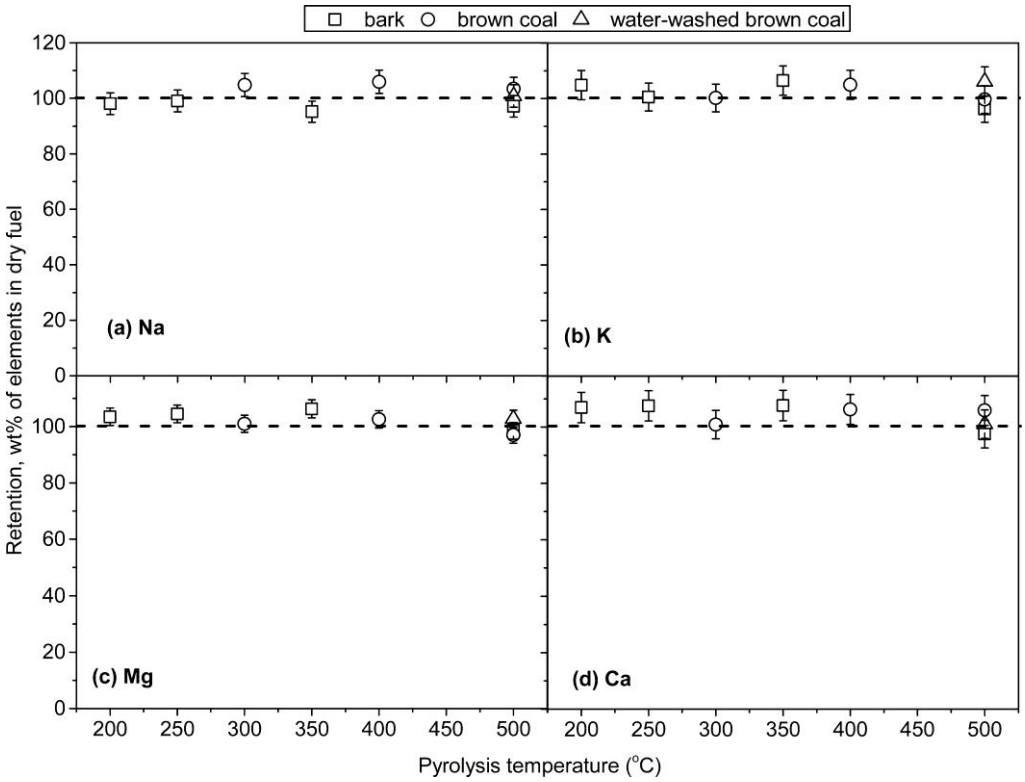

Figure 4-3: Retentions of (a) Na, (b) K, (c) Mg, and (d) Ca in the chars produced from the slow pyrolysis of the bark, brown coal, and water-washed brown coal samples, as a function of pyrolysis temperature.

The use of the two-step method at a pyrolysis temperature of 500 °C for quantifying Cl in low-rank solid fuels was then validated using the five standard samples (i.e., PVC, cellulose char, and three NaCl-loaded cellulose chars). Figure 4-4 depicts the results of method calibration using these standard samples. Close agreement between Cl contents quantified by the two-step method and their actual values clearly suggests that the method is indeed capable of quantifying Cl contents in low-rank solid fuels over a wide range (up to 567.3 mg/g fuel, db). The precision of the method was assessed by repeating at least 3 times for each standard sample. The relative standard errors are within 5%, indicating the high precision of the two-step method. Furthermore, Figure 4-4 also indicates that the two-step method is widely applicable for quantifying both inorganic and organic Cl in solid fuels, even in the

presence of abundant AAEM species.

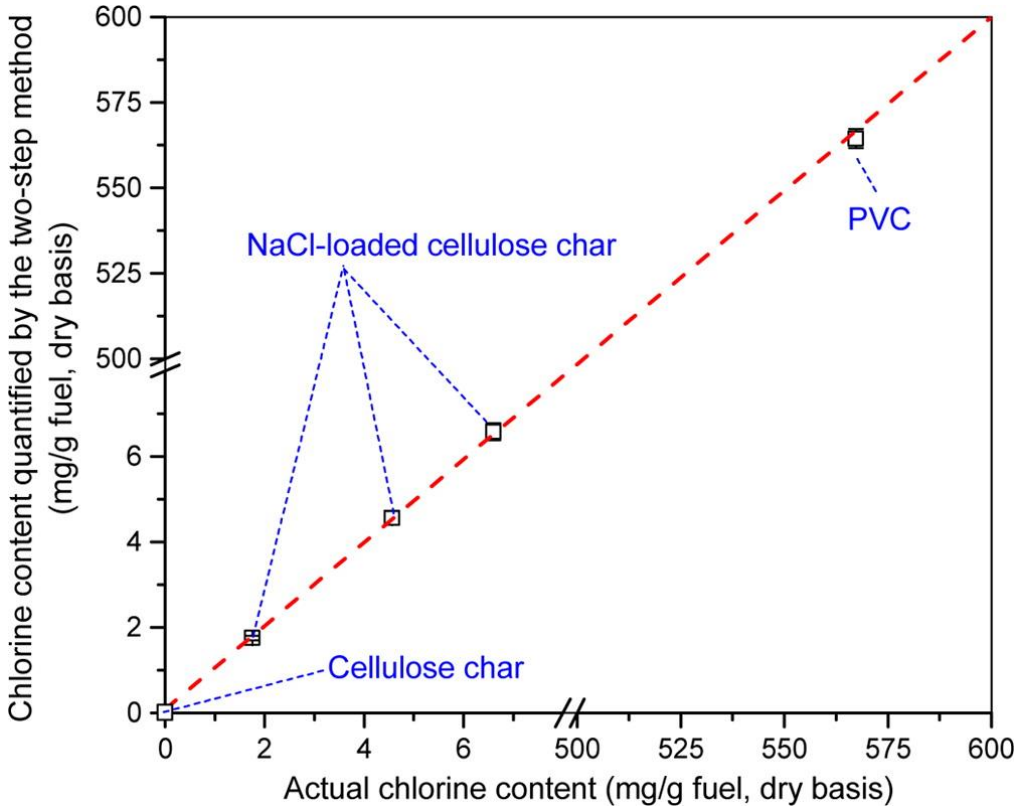

Figure 4-4: Comparison between the actual Cl contents in the standard samples and those quantified by the two-step method (at a pyrolysis temperature of 500 °C).

4.3. Application of the Two-Step Method for Quantifying Total Cl in Low-Rank Fuels.

Figure 4-5 illustrates the total Cl contents of the bark, brown coal, and water-washed brown coal samples, quantified by the two-step method. To investigate the effect of pyrolysis temperature, analysis using the two-step method was also carried out at lower pyrolysis temperatures (200–400 °C). There are three important findings from Figure 4-5. First, the Cl released into the volatiles during the bark pyrolysis increases rapidly from ~ 1.2 to ~ 4.0 mg/g fuel db with increasing temperature from 200 to 350 °C and levels off with further increasing temperature to 500 °C. Increasing pyrolysis temperature also intensifies Cl release during the brown coal pyrolysis, but to a lesser extent compared to that of the bark pyrolysis. For both the bark and the brown coal, the increase in the quantified Cl in the volatiles via the in situ

combustion method is clearly accompanied with the reduction in the quantified Cl in the corresponding char via the Eschka method.

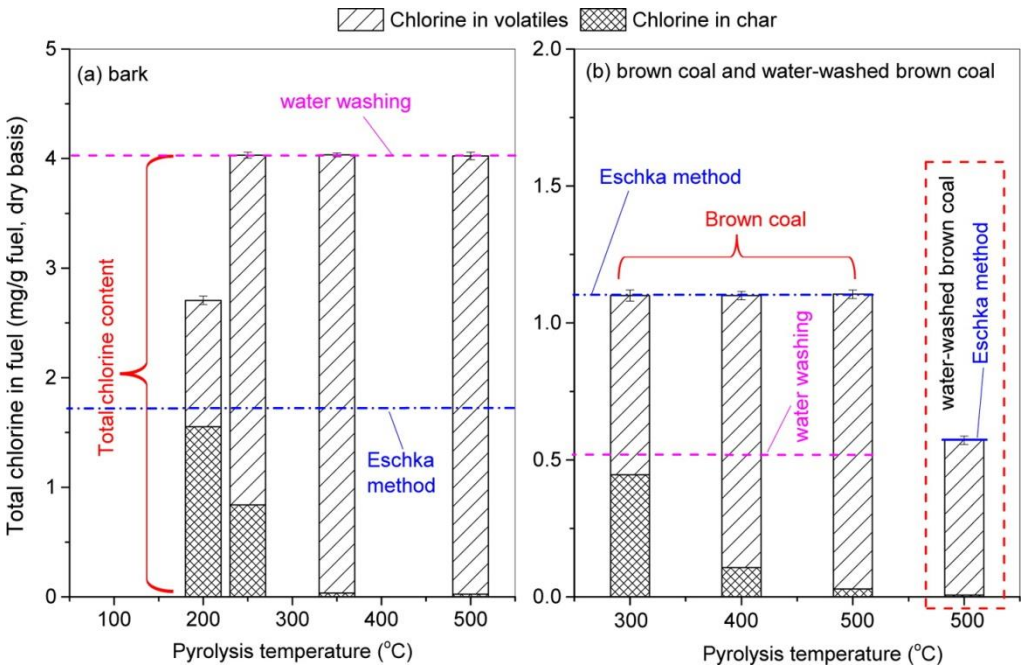

Figure 4-5: Total chlorine contents in the bark, brown coal and water-washed brown coal samples quantified by the two-step method benchmarking with those quantified by the water washing method and the Eschka method.

Second, the total Cl in the bark quantified by the two-step method is also sensitive to pyrolysis temperature. It increases from ~ 2.7 mg/g fuel db at 200 °C to ~ 4.0 mg/g fuel db at 250 °C and then levels off with further increasing temperature to 500 °C. The validation using the five standard samples demonstrates that as long as released into volatiles, Cl can be completely captured and quantified via the in situ combustion (see section 4.2). Therefore, the underestimation of the total Cl in the bark at a pyrolysis temperature of 200 °C must be due to Cl loss during the Eschka combustion. This is confirmed by comparing Cl content in bark–char–200 quantified by the Eschka method and that by the water-washing method, as shown in Figure 4-6. The sum of Cl in the bark–char–200 quantified by the water-washing method and Cl in volatiles produced at 200 °C gives a total Cl content of ~ 4.0 mg/g fuel db. This is similar to the Cl content analyzed using the two-step method at other pyrolysis

temperatures, indicating that after the pyrolysis of the bark at 200 °C, the Cl retained in char remains as water-soluble chlorides.

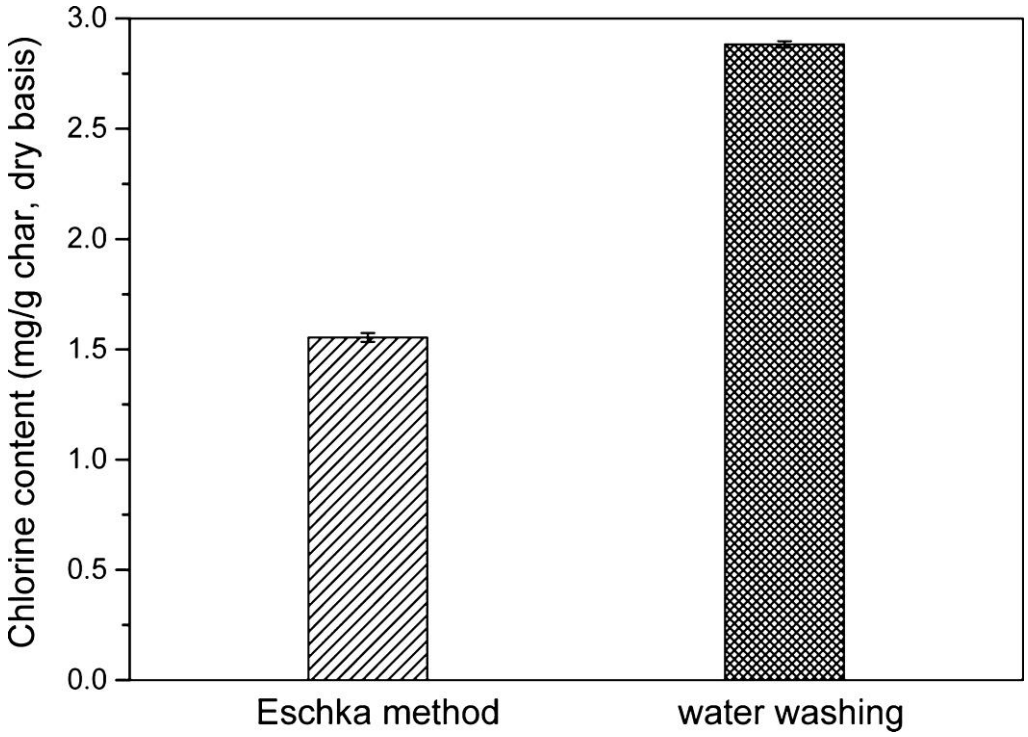

Figure 4-6: Comparison between Cl contents in bark char prepared from slow pyrolysis at 200 °C, quantified by the Eschka method and the water-washing method.

It is known that during the combustion of fuel and Eschka flux mixture, fuel Cl is retained in solid ash in form of chloride salts and/or possibly released into gas phase.[98] The Eschka flux would be only capable of trapping released HCl (g) while Cl released in other forms might escape from the Eschka flux bed.[98] Therefore, Cl loss during the Eschka combustion process is most likely due to the release of Cl into gas phase in forms other than HCl (g). It was also previously reported that the forms of Cl released are dependent on the stages of combustion process.[111] For example, during the early stages where the temperature is low and pyrolysis dominates, a significant amount of Cl can be released in forms other than HCl (g). (See chapter 7) Once char particles are ignited, during the char combustion stage, Cl is mainly released as HCl (g)[111] and/or retained in ash as solid chlorides under Eschka

combustion conditions. Therefore, the Cl loss during the Eschka combustion might be explained by the ignition temperature of the chars and their parent fuels.

Further efforts were thus made to determine the ignition temperatures of the bark, brown coal, and their derived chars sample using the TGA, following a method detailed elsewhere.[102] The ignition temperatures of the chars and their parent fuels are determined and plotted versus char preparation (pyrolysis) temperature (see Figure 4-7) to assess the stability of Cl in the chars before ignition. If the ignition temperature of a char is lower than its preparation (pyrolysis) temperature, then Cl in the char would be stable before ignition as the char has experienced a higher temperature during pyrolysis. Otherwise, Cl in the char would be released and likely in forms other than HCl (g) before ignition.

Indeed, for the bark–char–200, of which Cl content is significantly underestimated by the Eschka method, its ignition temperature (~263 °C) is considerably higher than its preparation temperature (200 °C). This means that, before the ignition of the char particles, further secondary pyrolysis would take place, during which Cl may be released in forms other than HCl (g). On the contrary, ignition temperatures of bark chars prepared at 250 and 350 °C are either close or lower than their preparation temperatures. The Cl in these chars is thus stable before ignition. Therefore, once these chars are ignited, the Cl would be either released as HCl (g) or retained in residue ash as chloride. Therefore, the Cl in these chars can be efficiently recovered by the Eschka method.

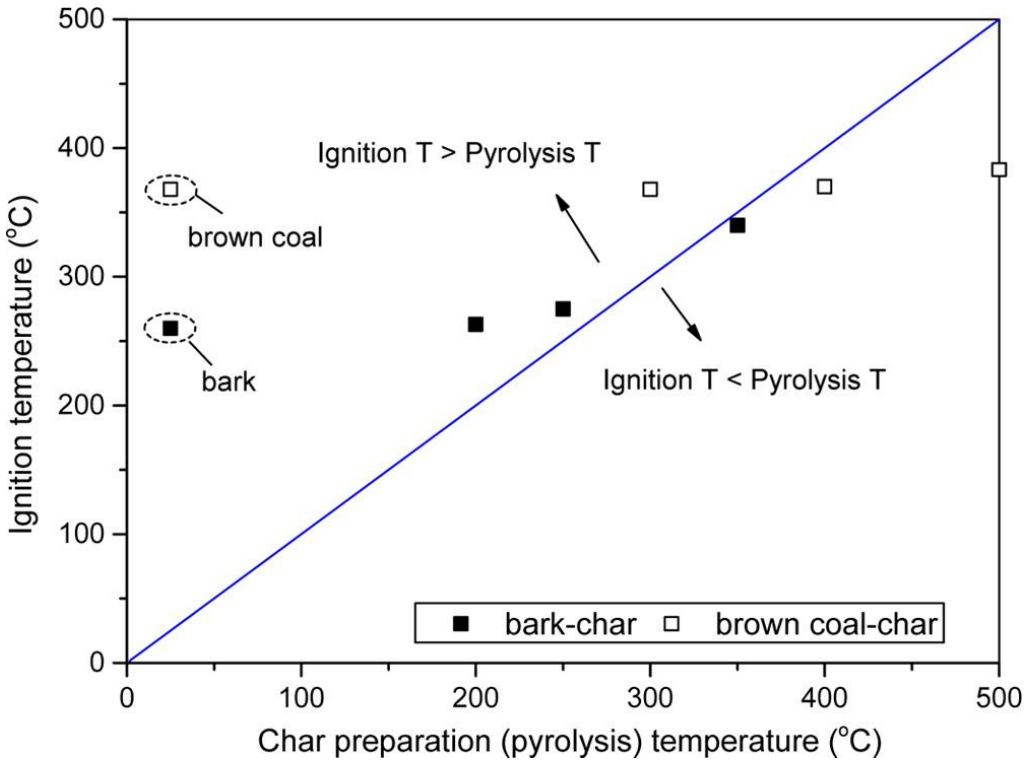

Figure 4-7: Comparison of ignition temperature of the char samples and their preparation (pyrolysis) temperature.

Third, the total Cl in the brown coal quantified by the two-step method is insensitive to pyrolysis temperature. Although the ignition temperature of the brown coal–char–300 is considerably higher than its preparation temperature, the Eschka method does not underestimate its Cl content. This can be explained by Cl release form during the brown coal pyrolysis. As shown in Figure 4-8, for the slow pyrolysis of the brown coal at 300 °C, the amount of Cl recovered in the volatiles, with and without volatiles in situ combustion is similar. This clearly indicates that during the pyrolysis of the brown coal Cl is mainly released as HCl (g) that can be effectively captured and subsequently quantified by the Eschka method. The release of HCl (g) during the pyrolysis of coals of various ranks was also reported in previous studies.[28, 86]

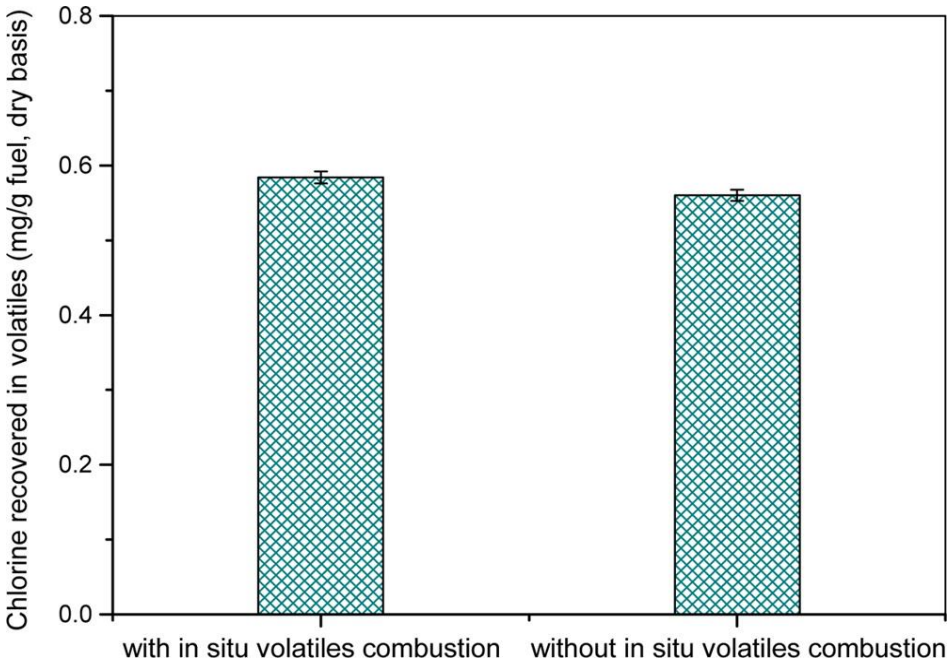

Figure 4-8: Cl recovered from volatiles during the pyrolysis of the brown coal at 300 °C with and without in situ combustion of volatiles.

Overall, the results in Figure 4-5 highlight that the choice of 500 °C as the pyrolysis temperature is essential to Cl quantification using the proposed two-step method. On one hand, such a pyrolysis temperature is sufficiently high (higher than 250 °C in this study for bark) to ensure that the Cl retained in char is stable enough to be quantified by the Eschka method. On the other hand, such a pyrolysis temperature ensures that 100% of AAEM species in the sample are retained in the char (see Figure 4-3). Thus, the Cl contents of the bark, brown coal, and water-washed brown coal samples quantified by the two-step method at 500 °C are reported as total Cl contents in these fuels, i.e. ~4.0, ~1.1, and ~0.6 mg/g fuel db, respectively.

4.4 Benchmarking of Two-Step Method against the Water-Washing and Eschka Methods

The Cl contents of the bark, brown coal, and water-washed brown coal samples quantified by the two-step method were then compared with those by the water-washing method and the Eschka method, respectively, as shown in Figure 4-5. For the bark, water washing gives similar Cl content to that determined by the

two-step method. This further confirms that that Cl in the bark is present mainly as inorganic chlorides. However, the applicability of the water washing method is largely dependent on the occurrences of Cl in fuel samples, i.e., only water-soluble chlorides in the fuels can be quantified. This is clearly demonstrated by the fact that the water washing of the brown coal significantly underestimates its total Cl content, because that part of Cl in the brown coal is present in water-insoluble forms.

The data in Figure 4-5 clearly show that compared to the two-step method, the Eschka method significantly underestimates the Cl content of the bark but gives similar Cl content of the brown coal. As discussed, the Cl loss during the Eschka combustion process of bark is most likely to be associated with the devolatilization (or pyrolysis) process that releases Cl in the forms other than HCl (g). Indeed, as shown in Figure 4-7, the ignition temperature of bark is ~260 °C, which means that a considerable amount of Cl would be released before sample ignition (see Figure 4-5). With respect to brown coal, Figure 4-8 clearly indicates that during the brown coal pyrolysis Cl is released as HCl (g) that can be captured by the Eschka method.

4.5 Conclusion

This work has developed a two-step method for the quantification of total Cl in low-rank solid fuels. The method has been validated by five standard samples and employed to quantify the total Cl in a bark, a brown coal, and a water-washed brown coal. Compared to the two-step method, the water-washing method yields similar result on the Cl content of the bark, in which Cl is present in water-soluble forms, but underestimates the Cl content of the brown coal samples due to the presence of water-insoluble Cl. While the conventional Eschka method can quantify the Cl content of the brown coal, it substantially underestimates the Cl content of the bark due to the Cl loss during Eschka combustion. Further investigation shows that in employing the two-step method, a pyrolysis temperature of 500 °C is suggested, at which the Cl loss during volatiles in situ combustion and char Eschka combustion can be avoided.

CHAPTER 5 DETERMINATION OF CL IN SOLID FUELS USING AN IMPROVED ESCHKA METHOD

5.1 Introduction

Thermochemical conversion of chlorine-containing solid fuels (e.g., coal,[27] biomass,[131] and refused derived fuels[132]) contributes significantly to the emission of hydrogen chloride,[133] chloromethane,[34] polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs),[35,134] and particulate matter,[135] which causes various environmental issues (e.g., acidic rain[136] and stratospheric ozone depletion[34]) and poses adverse impacts on human health. Accurate quantification of chlorine (Cl) in these fuels is obviously the fundamental requirement to understand the transformation behaviour of Cl during thermochemical processes and thereby mitigate environmental issues associated with its emission.

Conventional combustion based methods such as bomb combustion and Eschka methods, which are commonly used, encounter incomplete combustion[127] or the escape of Cl in forms other than gaseous hydrogen chloride HCl (g)[137] and thereby fail to accurately quantify Cl in solid fuels. To address these shortcomings, a novel two-step method was developed (see chapter 4). The method employed slow pyrolysis of a fuel at 500 °C to achieve the separation of fuel Cl. Cl released into volatiles was converted to HCl (g) via volatiles combustion, captured by sodium hydroxide (NaOH) solution, and quantified by ion chromatography (IC). Cl retained in char was quantified via conventional Eschka method. Although, the pyrolysis step stabilized Cl in char and ensured its complete capture by Eschka mixture (Sodium carbonate and magnesium oxide), it significantly prolonged the analytical time per sample and thus the efficiency of the two-step method was low. On the other hand, conventional Eschka method is time-efficient but has been proven to underestimate Cl content in the malle bark (see chapter 4).

Therefore, this part of project aims to develop a credible and time-efficient method for the quantification of Cl in various solid fuels, including biomass, coal, and polyvinyl chloride (PVC), on the basis of conventional Eschka method. The so-called "improved Eschka method" re-combusted the flue gas produced from the conventional Eschka combustion process, the Cl in which was converted into HCl (g), captured by 0.1 M NaOH solution, and quantified by IC. This key innovation enables the improved Eschka method to accurately quantify Cl in solid fuels via considering both Cl retained in solid after the Eschka combustion and that recovered in flue gas.

5.2 Drawbacks of Conventional Eschka Method

Figure 5-1a presents the Cl content of the five fuels determined by conventional Eschka method, benchmarking with that obtained by the two-step method. The Cl content determined by the two methods are in agreement for the three coal samples whereas Cl in the mallee bark and PVC samples quantified via conventional Eschka method is considerably lower than that from the two-step method. As it has been proved that the two-step method is capable of accurately quantifying total Cl in solid fuels (see chapter 4), conventional Eschka method clearly underestimates the Cl content in the mallee bark and PVC samples. There are two possible sources for such underestimation. One is the escaped Cl that is not captured by the Eschka mixture. The other is the possible incomplete recovery of Cl in the mixture of fuel ash and Eschka flux. However, dissolution in water and subsequent determination of Cl in the form of chlorides is known to quantify all the chlorine in coal ash and Eschka mixture[138, 139,] because all chlorides are water-soluble. Therefore, the Cl escaped from Eschka mixture is most likely the source of underestimation. Eschka mixture, which consists of sodium carbonate and magnesium oxide, might be only capable of capturing HCl (g) released during pyrolysis or combustion of fuels. Therefore, Cl released in forms other than HCl (g) may escape from the Eschka flux, which causes the underestimation of Cl when using conventional Eschka method.

Further efforts were made to summarize possible forms of Cl released during pyrolysis and combustion of coal, biomass and plastics reported in some previous studies,[25, 27, 29, 34, 43, 72, 89, 90, 92, 140-145] the results of which are presented in the Table 5-1. Depending on fuel types and temperatures experienced by fuel particles, Cl can be released in various forms such as HCl (g),[25, 27, 29, 43, 72, 90, 92, 140-145] gaseous potassium chloride KCl (g),[25, 29, 89, 90, 92, 140] chloromethane (CH3Cl),[34] and Cl organically bound with tar[142] during the pyrolysis and combustion of various coals, biomass and plastics. This provides some plausible explanations on the applicability of conventional Eschka method. HCl (g), which can be completely captured by Eschka flux, is the main form of Cl released during the pyrolysis and combustion of coals (see Table 5-1). Therefore, conventional Eschka method is capable of quantifying Cl in the three coals studied, which is demonstrated by the close agreement between Cl content determined by conventional Eschka method and the two-step method.

Table 5-1 also implies possible forms of Cl escaped during the combustion of the mixture of Eschka flux and the mallee bark (or the PVC). Apart from HCl (g), Cl can also be released as KCl (g), CH3Cl, and/or Cl organically bound with tar during biomass pyrolysis and combustion. KCl (g) is unlikely the possible form of Cl escaped from Eschka flux because its release temperatures (>700 °C, see Table 5-1), is higher than the combustion temperature (675 °C) of conventional Eschka method. On the other hand, the release CH3Cl and/or Cl organically bound with tar is likely the cause of underestimation of Cl content in the mallee bark via conventional Eschka method. This is supported by the temperature range (150 – 350 °C)[34] at which CH3Cl release takes place during biomass pyrolysis, which is in broad agreement with the ignition temperature (~260 °C) of the mallee bark shown in Figure 5-2.

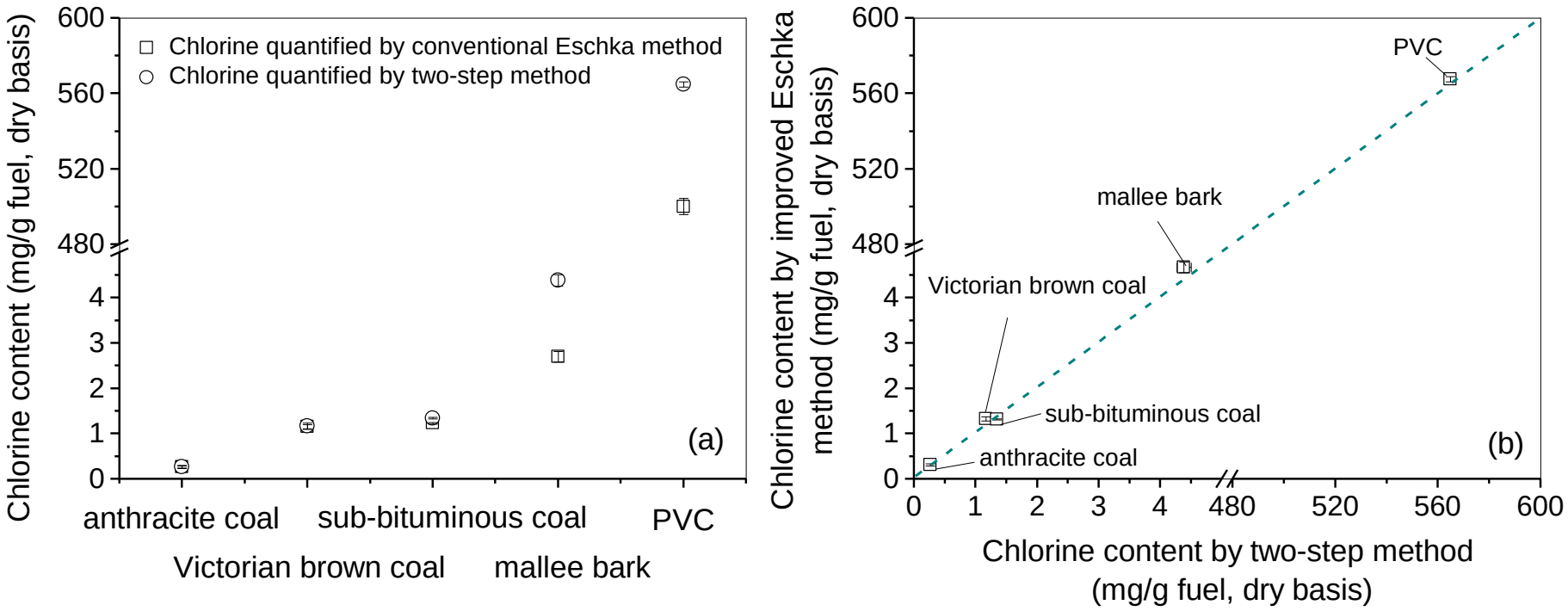

Figure 5-1. Benchmarking of chlorine contents in the mallee bark, Victorian brown coal, sub-bituminous coal, anthracite coal, and PVC samples determined by (a) conventional Eschka method and two-step method and (b) improved Eschka method and two-step method.

Table 5-1. Review on possible forms of chlorine release during pyrolysis and combustion of biomass, coal, and plastic fuels reported in some previous studies

Fuel category	Temperature (°C)	Directly identified (Yes/No)	Possible released forms	Reactive with Eschka flux (Yes/No)
Pyrolysis				
Forrest residue[a]	400 − 900	Yes	HCl (g)	Yes
	400 − 900	Yes	Cl in tar	No
	150 − 350[34]	Yes	CH3Cl	No
Agriculture residue[b]	500-700 [89], 400-700[25], 200-700[29],550-700[140]	No	HCl (g)	Yes
	700 − 1150[89], 700 − 1100[25], 700 − 900[29],700 − 900[140]	No	KCl	No
Lignite[c]	500-900[141]	Yes	HCl (g)	Yes
Sub-bituminous coal[d]	350 − 750[43]	Yes	HCl (g)	Yes
Bituminous coal[e]	300 − 600[72]	Yes	HCl (g)	Yes
Plastics[f]	260 − 300[142], 360 − 520[143]	Yes	HCl (g)	Yes
	260 − 300[142]	Yes	Chlorine in tar	No
Combustion				
Forrest residue[g]	500[90], 500[92]	No	HCl (g)	Yes
	> 700[90, 92]	No	KCl	No
Agriculture	500 − 700[89]	No	HCl (g)	Yes

residue[h]	700 − 1150[89]	No	KCl	No
Sub- bituminous coal[j]	200 − 1200[144]	Yes	HCl (g)	Yes
Bituminous coal[i]	210[27]	Yes	HCl (g)	Yes
Plastics[k]	150 − 600[145]	Yes	HCl (g)	Yes

[a] Detailed information on the samples used: mallee bark, leafs (cherry, oak, norway maple, beech) and wood (Eucalyptus delegatensis, Eucalyptus gunni, Beech, Horse Chestnut)[34] . [b]Detailed information on the samples used: wheat and carinata [89], wheat straw[25], sugarcane trash, switch grass, lucerne, straw (rape) [29], wheat straw pellets.[140] [c] Victorian brown coal.[141] [d] Indonesian, Chinese, and Australian sub-bituminous coal.[43] [e] Illinois coal.[72] [f] PVC.[142] [143] [g] wood[90], fibre board, bark.[92] [h] barley, rice, wheat, rape, oats and carinata.[89] [i] Thoresby Coals.[27] [j] Pindingshan coal mine.[144] [k] commercial PVC products[145]

Table 5-2. Proximate and ultimate analyses of fuels studied

Samples	Proximate Analysis (wt%, db[a])				Ultimate Analysis (wt%, daf[b])					
	Moisture[c]	VM[d]	Ash	FC[e]	C	H	N	S	Cl[f]	O
mallee bark	4.7	75.4	4.2	20.4	48.6	4.9	0.28	0.05	0.47	45.7
Victorian brown coal	5.9	51.6	1.6	46.8	65.2	5.3	0.57	0.26	0.13	28.5
sub-bituminous coal	1.1	27.3	21.2	49.5	81.8	5.0	1.45	4.45	0.13	7.2
anthracite coal	0.4	10.9	16.7	72.3	84.5	3.5	1.77	0.10	0.03	10.1

a Dry basis. b Dry Ash Free Basis. c Weight% Air-dried basis. d Volatile Matter. e Fixed Carbon.
f Quantified by Two-step method.

In other words, at least part of CH3Cl, which is unable to react with Eschka flux, would have been released before the ignition temperature of mallee bark is achieved. Similarly, part of Cl will be released into tar during the pyrolysis of PVC at 260 – 300 °C (see Table 5-1), which is responsible for the underestimation of Cl content in the PVC via conventional Eschka method because the Cl associated with tar is not reactive with Eschka flux.

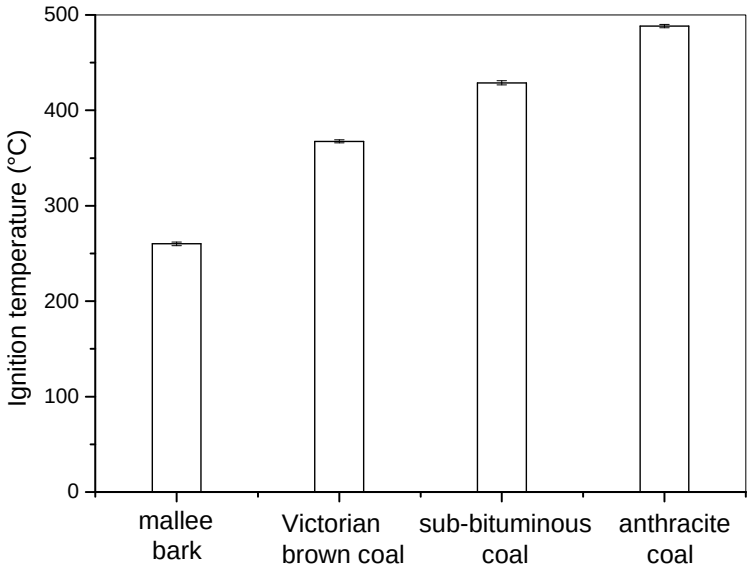

Figure 5-2. Ignition temperatures of the mallee bark, Victorian brown coal, sub-bituminous coal, and anthractite coal samples.

5-3 Development of the Improved Eschka Method

As the underestimation of Cl content in the mallee bark and the PVC via conventional Eschka method is mainly caused by the release (or escape) of Cl in forms other than HCl (g), the key to improve the conventional Eschka method is to re-capture and quantify the escaped Cl in flue gas. Figure 5-3 illustrates detailed design of the so-called improved Eschka method. The mixture of fuel and Eschka flux is combusted in air at 675 °C in the Eschka combustion column, following identical temperature program used by conventional Eschka method.[98] The combustion process separates fuel Cl into Cl retained in solid residue and that

released with flue gas. The Cl retained in solid residue includes solid chlorides in both fuel ash and Eschka flux and is quantified by dissolving the solid residue in ultra-pure water and subsequently determining chlorides in the solution by the IC. Cl escaped with the flue gas is converted into HCl (g) via in situ re-combustion of flue gas at 950 °C, captured by 0.1 M NaOH solution, and quantified by the IC. Therefore, the total Cl content of any given fuel is calculated by the equation below:

$$Cl_{(total)} = Cl_{(solid\ residue)} + Cl_{(flue\ gas)} \quad \text{(Eq. 5-1)}$$

where $Cl_{(total)}$ is the total Cl content in the fuel analysed. $Cl_{(solid\ residue)}$ is the Cl retained in solid residue whereas $Cl_{(flue\ gas)}$ is the Cl recovered by the re-combustion of flue gas.

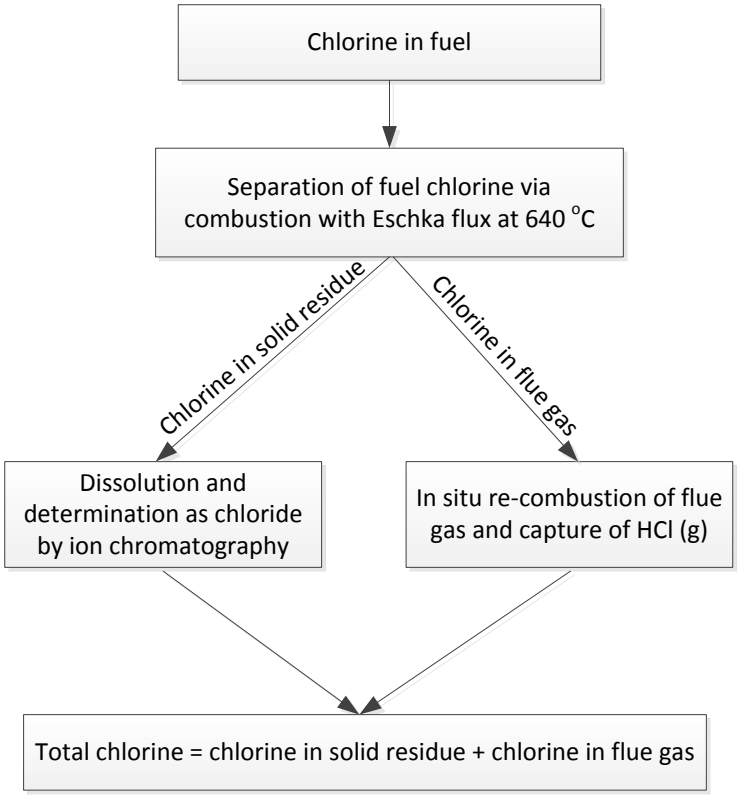

Figure 5-3: Design of the improved Eschka method for chlorine quantification.

5.4 Application of the Improved Eschka Method for the Quantification of Cl in Various Solid Fuels.

Figure 5-1b presents the Cl contents of the five fuel samples determined by the improved Eschka method, benchmarking with those from the two-step method. A close agreement between the Cl contents in all the fuels studied determined by the two methods validates the accuracy of the improved Eschka method. The improved Eschka method is capable of accurately quantifying Cl over a wide range (~0.3 – 567 mg/g fuel, dry basis) in various solid fuels such as biomass, coal, and plastics (mainly PVC), with a small relative standard error within ±2%. The distribution of Cl in the solid residue and flue gas is further presented in Figure 5-4. Whereas the Cl in flue gas is negligible for the three coals, ~48% and ~10% of Cl are presented in flue gas for the mallee bark and the PVC, respectively. This demonstrates that the underestimation of Cl contents in the mallee bark and the PVC via conventional Eschka method is indeed caused by the Cl released with flue gas. Most importantly, the complete recovery of Cl released with flue gas enables the improved Eschka method to accurately quantify Cl in the mallee bark and the PVC.

Further efforts were made to identify the form of Cl released with the flue gas during the combustion of the mixture of Eschka flux and the mallee bark at 675 °C. The Cl released with the flue gas was collected via 0.1 M NaOH solution in three different modes: (1) with flue gas in situ re-combustion; (2) without flue gas re-combustion; and (3) with the re-combustion of flue gas after condensing at 110 °C. The first mode is capable of quantifying total Cl released with volatiles whereas the second one only collects the HCl (g) escaped from the Eschka flux (if any). In the third mode, the temperature of the bottom connection tube between the Eschka combustion column and the flue gas re-combustion column was set at 110 °C because this temperature is sufficiently low to allow the condensation of heavy unburned organic compounds (if any) but high enough to avoid moisture condensation which can trap HCl (g) and CH_3Cl (g) in the flue gas. Therefore, only light unburned organic compounds and/or

CH_3Cl (g) in the flue gas will be re-combusted and quantified. The results are presented in Figure 5-5, with two important findings observed. First, Eschka flux is capable of capturing all the Cl released as HCl (g) during the combustion of the mixture of Eschka flux and the bark. This is supported by two facts. One is that, in the second mode, the flue was kept at ~500 °C before entering the gas bubbler to avoid any HCl (g) loss as a result of moisture condensation. The other is that negligible Cl in the flue gas is collected without flue gas combustion (see Figure 5-5). Second and last, ~60% of the Cl in the flue gas is still captured after condensation at 110 °C, indicating that the Cl escaped with the flue gas is not only in association with heavy unburned organic compounds but also in the forms of light organic compounds and/or gas (e.g., CH3Cl[55]).

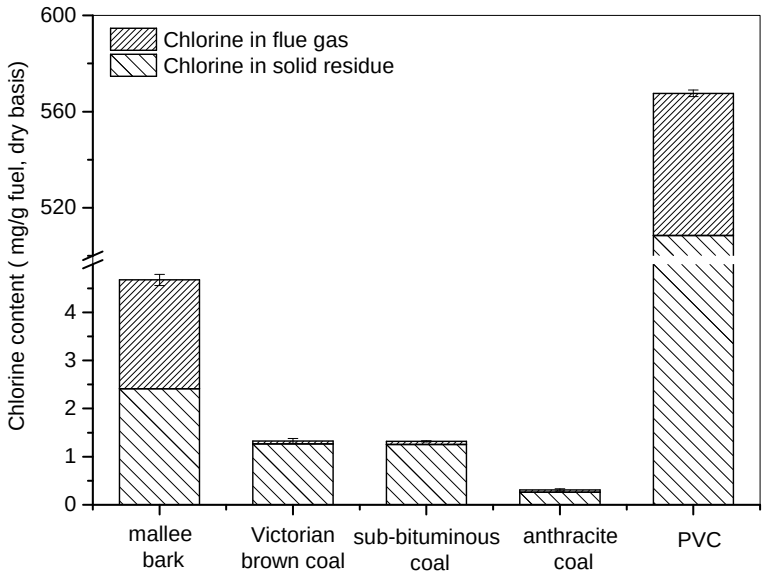

Figure 5-4: Distribution of chlorine in solid residue and flue gas quantified via improved Eschka method.

Although both the improved Eschka method and the two-step method are capable of quantifying Cl in various solid fuels such as biomass, coal, and plastics, the former one possesses two advantages over the later one, i.e. a shorter analytical time per sample and a smaller relative standard error (see Table 5-3). This is because that the

improved Eschka method omits the pyrolysis step, which is employed in the two-step method.

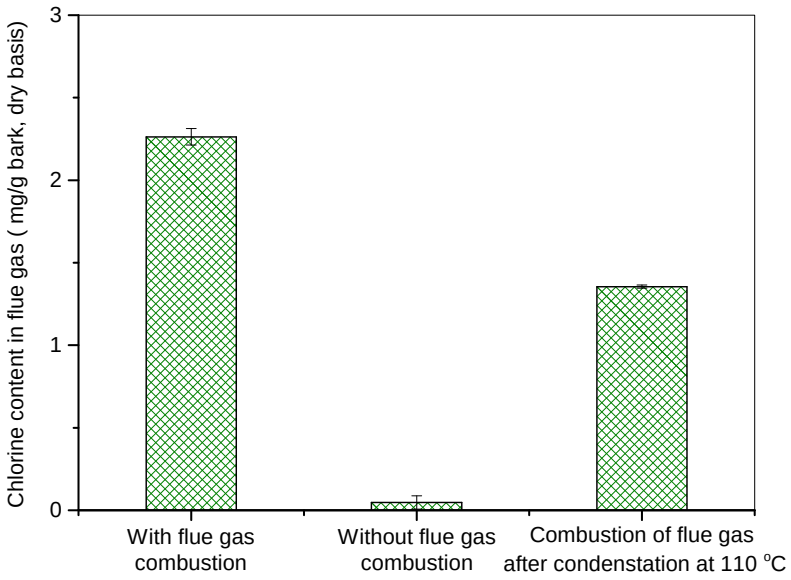

Figure 5-5: Chlorine content recovered in flue gas during Eschka combustion of the mallee bark.

Table 5-3: Comparison of improved Eschka method and two-step method

Method	Applicability	No. of Analytical Steps	Time Requirement	Relative Standard error
Two-Step Method	Coal, Biomass and Plastics	2	~6 hr	< 5%
Improved Eschka Method	Coal, Biomass and Plastics	1	~3 hr	< 2%

5.4 Conclusion

Compared to the two-step method, the improved Eschka method possesses at least two advantages, although both methods are capable of accurately quantifying Cl in various solid fuels. One is that the analytical time is shortened from ≥8 h for the two-step method to ≤3 h for the improved Eschka method. The other advantage is that the relative standard error (±2%) for the improved Eschka method is much smaller than that (±5%) of the two-step method. Such advantages are because the improved Eschka method omits the lengthy pyrolysis step that is otherwise essential in the two-step method.

CHAPTER 6 RELEASE OF CL FROM THE SLOW PYROLYSIS OF NACL-LOADED CELLULOSE AT LOW TEMPERATURES

6.1 Introduction

Biomass contains abundant Cl[146] that is known to be notorious during thermochemical processing for various ash-related problems including ash deposition,[147] corrosion,[148] and particulate matter emission.[135] The occurrence form of Cl in biomass is reported to be mainly water-soluble form [25] and the release of Cl during pyrolysis is temperature-dependent. [25, 90, 92, 146, 149] A significant amount of Cl (e.g., up to ~60%, see Fig. 6-1) can be released at low temperatures (≤500 °C) and the remaining Cl is released at high temperatures (e.g., 700−800 °C). [89] It is well documented that the high-temperature Cl release is a result of alkali chlorides evaporation and/or its interaction with other inorganic species (e.g., aluminosilicates) in biomass. [146] However, the low-temperature Cl release is poorly understood. Although two possible mechanisms, i.e., ion-exchange reaction between solid alkali chlorides and proton-donating groups (e.g., carboxylic groups) [90, 92] and direct transfer of Cl to a liquid tar phase,[25] have been hypothesized, no convincing evidences were provided.

There are two challenges in obtaining a thorough understanding on the low-temperature Cl release mechanisms during biomass pyrolysis. One is the complexity of biomass macromolecular structure and the other is the difficulty in achieving a satisfied Cl mass balance during pyrolysis. The first challenge can be partly addressed by using cellulose (a major component in biomass[150]) as a model compound because its structure is relatively simple and pyrolysis mechanisms have been well studied.[151] A pioneering study[149] has demonstrated the release of Cl from the slow pyrolysis of KCl-loaded cellulose but did not report the forms of Cl released and its distribution in pyrolysis products (i.e., gas, tar, and char) because it quantified

the Cl release based on its retention in char only. The second challenge is due to the fact that conventional Cl quantification methods (e.g., Eschka method) are unable to accurately quantify Cl in biomass and its derived chars produced at low temperature (e.g., 200 °C) . Direct quantification of Cl released is also difficult due to the complicated forms (e.g., HCl and/or organically bound to volatiles) of the Cl released. The improved Eschka method developed by the same authors has paved the way in achieving a satisfied Cl mass balance during biomass pyrolysis.

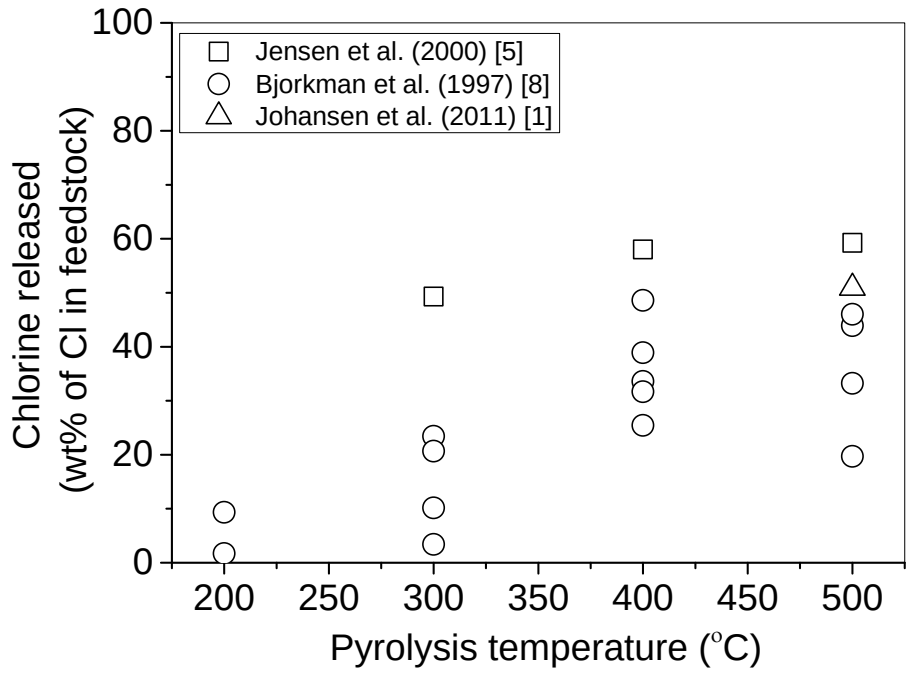

Fig. 6-1: Release of Cl during slow pyrolysis of various biomass materials at temperatures below 500 °C, as reported in previous studies[25, 146, 149]. .

Consequently, this study carries out a systematic investigation into the release of Cl from the slow pyrolysis of NaCl-loaded cellulose at low temperatures, aiming at providing new data for better understanding on the low-temperature Cl release during biomass pyrolysis. A NaCl-loaded cellulose (Cl loading level: ~2.0 mg Cl/g cellulose, dry basis) was pyrolysed at 150−400 °C. A two-column pyrolysis/combustion reactor system was used, enabling the quantification of the Cl released from pyrolysis with or without volatiles combustion. The Cl retained in the solid residues was quantified

using the novel two-step method recently developed in our previous study. A Cl mass balance close to 100% was achieved.

6.2 Weight Loss and Cl Mass Balance in Volatiles and Solid Residues during the Pyrolysis of the Nacl-Loaded Cellulose

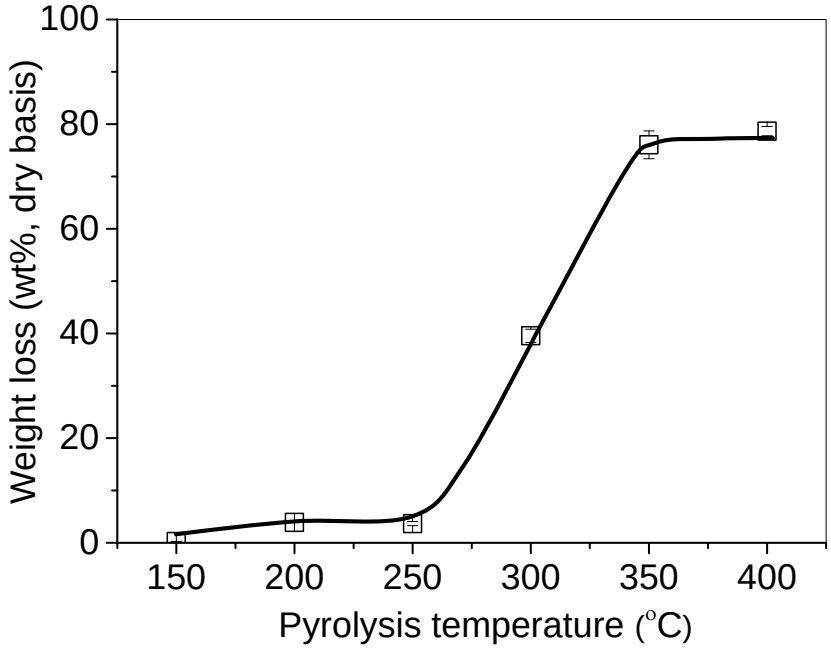

Fig. 6-2: Weight loss during the slow pyrolysis of the NaCl-loaded cellulose at 150−400 °C.

Fig. 6-2 presents the weight loss during slow pyrolysis of the NaCl-loaded cellulose as a function of pyrolysis temperature, based on dry basis. It can be seen that the weight loss begins at 200 °C, experiences a rapid increase at temperatures from 250 °C (~4 wt%) to 350 °C (~76 wt%), and then levels off with further increasing temperature to 400 °C. The weight loss profile is slightly different with the one reported in a previous study[152] on the fast pyrolysis of NaCl-loaded cellulose because of different pyrolysis conditions (e.g., the loading level of NaCl, heating rate, and holding time) employed. Nevertheless, the significant weight loss shown in Fig. 6-2 implies that it is very likely that part of Cl in the NaCl-loaded cellulose might be released with the evolution of volatiles during pyrolysis. Further analysis was then

carried out to investigate the mass balance of Cl released into the volatiles and that retained in the solid residues from the slow pyrolysis of the NaCl-loaded cellulose at 150−400 °C. As shown in Fig.6-3, indeed, up to ~75% of Cl in the NaCl-loaded cellulose is released into the volatiles at 400 °C. Most importantly, a Cl mass balance close to 100% is achieved, demonstrating that the methods used in this study (i.e., volatiles in situ combustion and the improved Eschka method) are capable of quantifying the Cl released into the volatiles and that retained in the solid residues after pyrolysis. This enables us to systematically investigate the Cl release and its distribution among the gases, tar, and solid residues from the slow pyrolysis of the NaCl-loaded cellulose.

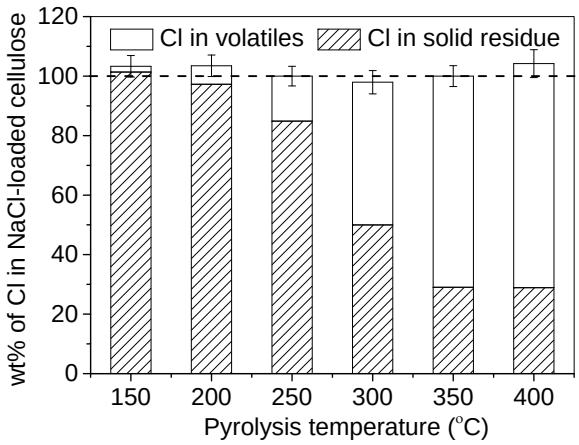

Fig.6-3. Mass balance of Cl released into volatiles and that retained in the solid residues from the slow pyrolysis of the NaCl-loaded cellulose at 150−400 °C.

6.3 Forms of Cl Released in The Volatiles and Retained in the Solid Residues During the Pyrolysis of the Nacl-Loaded Cellulose

Fig. 6-4 presents the data on Cl released into the volatiles during the slow pyrolysis of the NaCl-loaded cellulose as a function of pyrolysis temperature, with or without volatiles in situ combustion. In the case of with volatiles combustion, all Cl released into the volatiles is converted into gaseous chloride (i.e., HCl) and quantified. It is obvious that, Cl2 and HCl are the only Cl-containing gases that can react with NaOH solution. Previous studies[153, 154] suggest that no Cl2 is released during biomass

pyrolysis (or devolatilization) using online instruments such as molecular beam mass spectrometry (MBMS). Therefore, in the case of without volatiles combustion, the Cl collected in the NaOH solution is in form of HCl (g). As shown in Fig. 6-4, both the form and the amount of Cl released into the volatiles are sensitive to pyrolysis temperature. It can be seen that Cl is mainly released as HCl (g) at temperatures below 300 °C, whereas it is clearly evident that further increase in pyrolysis temperature results in the release of Cl in forms other than HCl (g). Furthermore, the release of both total Cl and HCl (g) in the volatiles, as quantified in the cases of with or without volatiles combustion, commences at 200 °C, becomes significant between 250 and 350 °C, and then levels off with further increasing temperature to 400 °C. As a result, ~71−75% and ~53−56% of the Cl in the NaCl-loaded cellulose are released into volatiles at 350−400 °C as total Cl and HCl (g), respectively. Therefore, the release of Cl (~19% of the Cl in the NaCl-loaded cellulose) in forms other than HCl (g) is clearly evidenced under the two experimental conditions.

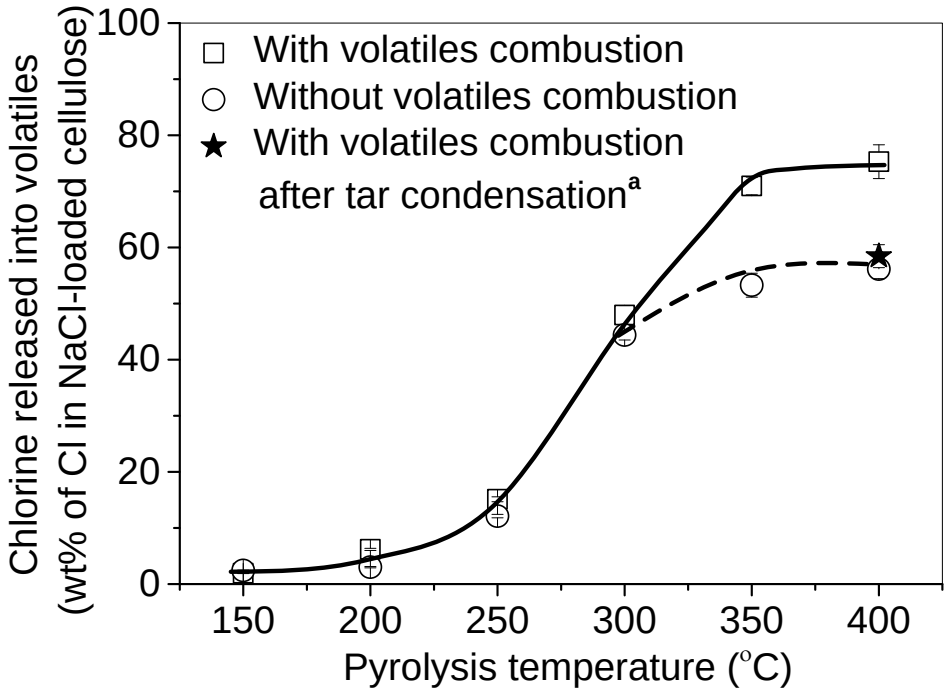

Fig. 6-4. Cl released into volatiles from the slow pyrolysis of the NaCl-loaded cellulose at 150−400 °C. a The light volatiles are combusted after the condensation of heavy tar at 110 °C.

Further efforts were then made to identify the form of the non-HCl (g) Cl released at 400 °C. By adjusting the temperature of the bottom connection tube between the pyrolysis column and the combustion column, the volatiles produced from the slow pyrolysis of NaCl-loaded cellulose at 400 °C were condensed at 110 °C. This condensation temperature is sufficiently low to condense heavy tar but avoids the loss of HCl (g) due to water condensation. The light volatiles (including light tar and non-condensable gases), which were not condensed at 110 °C, were in situ combusted in the combustion column at 950 °C to quantify the total Cl that had escaped after heavy tar condensation. The data is also plotted in Fig. 6-4. It can be seen that the total Cl in the light volatiles is almost identical to the amount of HCl (g) released at 400 °C, leading to two important findings. One is that HCl (g) is the only Cl-containing gas released into volatiles during the slow pyrolysis of the NaCl-loaded cellulose. It should be noted that Hamilton et al [34] reported the release

of gaseous chloromethane (CH3Cl) during biomass pyrolysis at temperatures below 350 °C. However, the data in this study do not support the formation of CH3Cl during the slow pyrolysis of the NaCl-loaded cellulose. This is not surprising because the NaCl-loaded cellulose does not contain pectin, which is proposed as the major CH3 donor for the formation of CH3Cl during biomass pyrolysis [34]. The other is that the Cl released in forms of non-HCl (g) is organically bound in heavy tar (termed as "tar-Cl" hereafter) that can be condensed at 110 °C. This is confirmed by the fact that, this part of Cl can be converted to HCl (g) via the combustion of the whole volatiles (including both the heavy tar and the light volatiles) but cannot be quantified in the case of the light volatiles combustion only. It should be noted that the release of tar-Cl in volatiles has thus far not been reported in open literature during the pyrolysis of Cl-loaded cellulose.

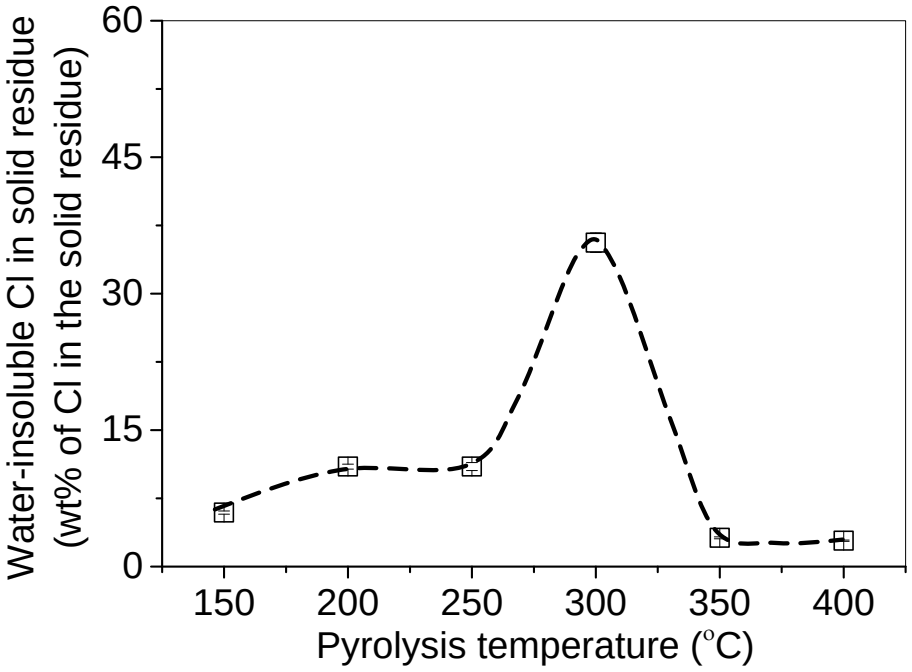

Fig.6-5. Water-insoluble Cl in the solid residues produced from the slow pyrolysis of the NaCl-loaded cellulose at 150−400 °C.

Fig. 6-5 presents the amount of water-insoluble Cl retained in the solid residues after the slow pyrolysis of the NaCl-loaded cellulose at 150−400 °C, expressed as wt% of

the Cl in the solid residues. Whereas all the Cl in the NaCl-loaded cellulose can be washed out by water at room temperature, an appreciable amount (~5%) of water-insoluble Cl is present in the solid residue produced at a pyrolysis temperature as low as 150 °C. The amount of water-insoluble Cl in the solid residues increases with increasing pyrolysis temperature, peaks at 300 °C (~36% of the Cl in the solid residue), and then drastically decreases with further increasing pyrolysis temperature to 350−400 °C. The data suggest that at least part of Cl is organically bound to the organic structure of the solid residues and such organic bonds are thermally instable because increasing pyrolysis temperature to 350−400 °C results in the disappearance of the organically bound Cl in the solid residues. While the exact mechanisms responsible for the incorporation of Cl into the organic structure of the solid residues remain unclear, there are at least two possibilities. One is that Cl may incorporate in aliphatic open chain fragments produced from fragmentation reaction during cellulose thermal decomposition [155]. The other is the intra- and inter-particle interactions between HCl (g) and the molten reaction intermediates (that can be formed during cellulose pyrolysis [156]) on the surface of pyrolysing cellulose particles before the HCl (g) leaves the sample bed. Further studies are required to reveal the mechanisms that lead to the incorporation of Cl in the organic structure of the solid residues.

6.4 Further Discussion on Cl Release During the Pyrolysis of Nacl-Loaded Cellulose at Low Temperatures

Overall, the data in Figs. 6-4 and 6-5 demonstrate that increasing pyrolysis temperature from 150 to 300 °C leads to the substantial release of Cl in form of HCl (g), accompanied with the incorporation of the Cl retained in the organic structure of the solid residues. Further increasing pyrolysis temperature to 350−400 °C results in the release of the tar Cl and the depletion of organically bound Cl in the solid residues. The results suggest that depending on pyrolysis temperature, different mechanisms are responsible for Cl release during the slow pyrolysis of the

NaCl-loaded cellulose. These mechanisms are discussed as follows.

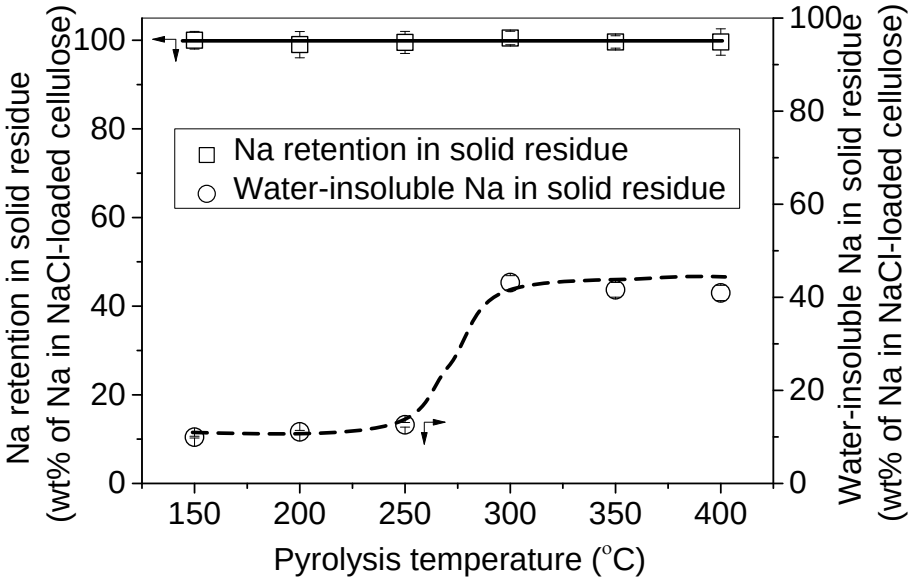

Fig. 6-6. Na retention and amount of water-insoluble Na in the solid residues produced from the slow pyrolysis of the NaCl-loaded cellulose at 150−400 °C.

The form of Cl in the NaCl-loaded cellulose is believed to play significant role in the HCl (g) release during pyrolysis. Although the exact form of Cl after drying the NaCl-loaded cellulose remains unknown, it is unlikely presented as NaCl molecules. To prove this point, a solid mixture of dry cellulose and NaCl particles were prepared, the Cl content in which is identical with that in the NaCl-loaded cellulose prepared via wet impregnation. No HCl (g) release is observed from the slow pyrolysis of the mixture of dry cellulose and NaCl particles at 200 °C whereas HCl (g) release has commenced at the same temperature for the pyrolysis of the NaCl-loaded cellulose (see Fig. 6-4). Most likely, after wet impregnation, the drying the NaCl-loaded cellulose may lead to Na forming a coordination bond with oxygen in the cellulose structure [156, 157] while Cl might act as H-bond acceptor that interacts with the hydroxyl group in cellulose [158]. Upon heating, the breakage of hydroxyl group, which is associated with dehydration reaction, would result in the release of HCl (g). This possible mechanism is supported by two indirect pieces of evidences. One is the elemental hydrogen (H) release data calculated based on the weight loss

(see Fig. 6-2) and H content in the solid residues. The data show that ~6% of H has been released at 200 °C, indicating that dehydration reaction indeed takes place at relatively low temperature [159]. Such a temperature (i.e., 200 °C) coincides with the onset temperature where HCl (g) starts to release (see Fig. 6-4). The other piece of evidence is that along with the release of HCl (g) during the slow pyrolysis of the NaCl-loaded cellulose, at least part of Na would be bound to the organic structure of the solid residues and thereby become water-insoluble. This is exactly the case shown in Fig. 6-6. Na retention during the slow pyrolysis of the NaCl-loaded cellulose is close to 100% but up to ~43% of total Na in the NaCl-loaded cellulose has become water-insoluble after pyrolysis.

It is also noted that the release of the organic tar-Cl takes place at a narrow temperature range of 300−350 °C. Although the possibility of gas phase reactions between HCl (g) and volatiles cannot be ruled out, it is most likely that the tar-Cl originates from the Cl that is organically incorporated into the solid residues. Indeed, the appearance of tar-Cl in the release volatiles correlates well with the depletion of organically bound Cl in the solid residue when increasing pyrolysis temperature from 300 to 350 °C. Overall, the results in this study clearly demonstrate that interactions between Cl and cellulose organic structure are responsible for the release of both HCl (g) and organic tar Cl during the slow pyrolysis of biomass at low temperatures (e.g., ≤400 °C).

6.5 Conclusion

Cl is mainly released as HCl (g) from the slow pyrolysis of the NaCl-loaded cellulose at temperatures below 300 °C. Further increase in the pyrolysis temperature results in the release of Cl in the form of organically bound into tar (ie tar-Cl). The release of both HCl (g) and total Cl (including gaseous HCl and tar-Cl) commences at 200 °C, reaches the maximum at 350 °C, and then levels off with further increasing temperature to 400 °C. An increase in the pyrolysis temperature from 150 to 300 °C leads to a considerable increase in the amount of organically bound Cl in

the solid residues whereas further increasing temperature to 350−400 °C leads to its depletion in the solid residues.

CHAPTER 7 RELEASE OF Cl DURING MALLEE BARK PYROLYSIS

7.1 Introduction

Mallee biomass, as a byproduct of managing dryland salinity that seriously threatens the premium agricultural lands in Western Australia, is considered to be a key second-generation lignocellulosic feedstock projected for future bioenergy supply in the state.[8, 9, 21, 160] One important feature of mallee is the presence of abundant Cl and other inorganic species (such as alkali and alkaline earth metallic (AAEM) species, mainly Na, K, Mg, and Ca) concentrated mainly in bark and leaf.[19] The released Cl is known to be responsible for various ash-related issues[32, 33, 161, 162] during combustion or gasification. In the application of biomass pyrolysis for bio-oil and biochar production, these species are important considerations as well. For instance, the presence of Cl and other inorganic species is an important parameter in the specifications of using these high-energy-density fuels for subsequent energy applications.[23, 163-166] On the other hand, if retained in biochar, Cl (a plant micronutrient) and other nutrient species may be recycled for plant growth when biochar is returned to the field for soil amendment and carbon sequestration.[19] Therefore, a thorough understanding on the release of Cl during pyrolysis is essential to developing technologies for biomass use.

During biomass pyrolysis under slow heating rate, the release of Cl was reported to be temperature-dependent, with a significant amount of Cl released between 200 and 500 °C[19, 90, 92] and the remaining Cl released around 800 °C.[25, 29, 94, 167] Cl release also largely depends upon its mode of occurrence in biomass during pyrolysis. Accordingly, it was proposed that organic Cl transfers to tar first and then possibly releases to the gaseous phase as HCl (g).[90, 92, 94] Inorganic Cl was speculated to release as HCl(g) below 500 °C through either ion-exchange reactions between solid potassium chloride KCl(s) and proton-donating sites (e.g., carboxylic groups) [90, 92,

[94] or direct transfer of Cl to a liquid tar phase,[25] depending upon assumptions for the type of inorganic Cl after biomass drying. Also notably, previous studies[99, 141] on brown coal pyrolysis suggested that the prolonged volatile–char interactions play important roles in the release of Cl and AAEM species during the pyrolysis of Loy Yang brown coal in a fluidized-bed/fixed-bed reactor. However, the release of Cl in those previous studies was mainly based on the quantification of Cl retentions in chars. Little work has been performed on direct quantification of Cl in volatiles (including Cl in gas and Cl in tar). Also, the in situ experimental quantification of Cl in tars has received little attention. Clearly, experimental data and knowledge on these aspects are critical toward not only understanding Cl release mechanisms during biomass pyrolysis but also for biomass to energy conversion applications.

Therefore, the primary objective of this study is to carry out a systematic investigation on the release of Cl during the pyrolysis of mallee bark under a wide range of temperatures and reactor configurations. Three types of reactor configurations are considered, including a fixed-bed reactor and a drop-tube/fixed-bed reactor (with either continuous or pulsed feeding). Distributions of Cl among various biomass pyrolysis products are reported. Cl in gas phase and Cl in tar are successfully quantified using a two-column pyrolysis/combustion reactor.

7.2 Mode of Occurrence of Cl in Biomass

Inorganic elements (e.g., Cl and AAEM species) in solid fuels may exist as free ions in aqueous solution in pores, distribute as discrete salt/mineral particles, and/or bond organically to carbonaceous material in the fuel.[90, 92, 168] To understand the mode of occurrence of these inorganic species, the raw biomass sample was first subject to water leaching to quantify water-soluble species, the result of which is presented in Figure 7-1. The initial concentrations of Cl and other inorganic species in the biomass are presented in Table 7-1. It should be noted that, in this study, the water leaching was carried out using a semi-continuous leaching apparatus that rapidly swept the leachate out of the reactor, with the biomass particles remaining on the frit

inside the reactor. Such leaching has a unique feature of minimizing the contact between the leachate and the biomass particles being leached, offering significant advantage over the conventional batch leaching process commonly used in such applications. The leachate from batch leaching of biomass with water contains acidic organic matter that may, in turn, interact with the biomass matrix to leach out part of organically bound inorganic species. As shown in Figure 7-1, 100% of Cl, 88% of Na, 95% of K, and 55% of Mg in biomass are water-soluble but only ~ 5.5% of Ca in biomass can be leached by water. The results suggest that all Cl species in raw biomass exist as either free ions in aqueous solution and/or deposit as discrete water-soluble salt particles, such as alkali chlorides.

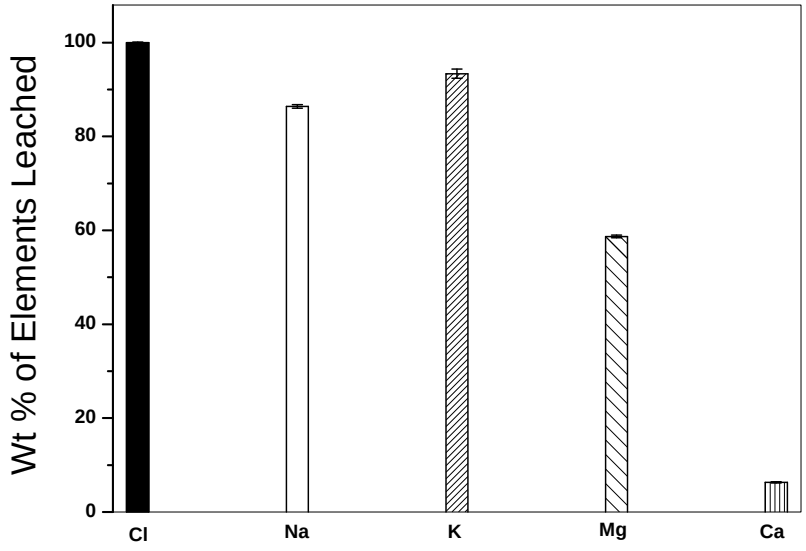

Figure 7-1 Mass percentage of water-soluble elements leached from the raw biomass via water leaching.

Table 7-1: Proximate and ultimate analysis of raw biomass and its derived chars prepared under various conditions (FB-Char-XXX, Char prepared under fixed-bed reactor configuration at XXX oC; CFDT/FB-Char-XXX, Char prepared in Continuous-Feeding Drop-tube/fixed-bed configuration at XXX ^{o}C; PFDT/FB-Char-XXX, in Pulse-Feeding Drop-tube/fixed-bed configuration at XXX ^{o}C)

Samples	Moisture (wt%, ad)	Proximate Analysis (wt%,db)			Ultimate Analysis (wt%, daf)						Contents of AAEM species (wt%, db)			
		VM[a]	Ash	FC[b]	C	H	N	S	Cl	O[c]	Na	K	Mg	Ca
Raw Bark	5.7	77.3	4.7	18	48.92	4.97	0.23	0.03	0.41	45.44	0.1364	0.2589	0.2062	1.3677
FB-Char-400	6.0	36	10.8	53.2	73.71	2.94	0.62	0.02	0.01	22.69	0.3833	0.7055	0.5711	3.7948
FB-Char-500	4.4	26.1	13.6	60.3	73.33	2.81	0.55	0.02	0.01	23.28	0.4628	0.8704	0.7096	4.6583
FB-Char-600	3.8	21.7	13.4	64.9	87.83	1.86	0.59	0.01	0.01	9.70	0.4947	0.9543	0.7762	5.0640
FB-Char-700	3.9	18.7	14.5	66.8	92.37	0.99	0.58	0.01	0.01	6.03	0.4786	0.9903	0.8177	5.0935
FB-Char-800	3.8	17	14.5	68.5	93.54	1.07	0.78	0.01	0.01	4.60	0.4551	1.0176	0.8328	5.0616
FB-Char-900	3.4	15.6	15.1	69.3	94.32	0.69	0.64	0.01	0.01	4.34	0.4274	0.9454	0.7687	4.9628
CFDT/FB-Char -400	6.0	43.3	11.1	45.6	69.31	3.74	0.55	0.02	0.01	26.37	0.4302	0.6907	0.6463	4.1725
CFDT/FB-Char -500	6.3	32.4	17.9	49.7	75.83	2.35	0.57	0.04	0.56	20.65	0.5788	0.9432	0.8646	5.5712
CFDT/FB-Char -600	3.2	21.9	18	60.1	82.67	1.73	0.50	0.07	1.01	14.02	0.6313	1.0433	0.9763	6.3093
CFDT/FB-Char -700	2.2	18.6	21.2	60.2	81.39	1.32	0.35	0.06	1.02	15.86	0.5567	1.0325	0.9838	6.4913

CFDT/FB-Char -800	3.0	19.6	20.3	60.1	89.82	0.89	0.43	0.07	0.67	8.13	0.3957	0.9703	0.9856	6.4693
CFDT/FB-Char -900	2.6	16.5	29.5	54	93.54	1.77	0.63	0.07	0.30	3.48	0.2848	0.8891	1.4732	9.9793
PFDT/FB-Char -400	6.4	35.8	15.6	48.6	72.80	3.10	0.64	0.10	0.03	23.34	0.4353	0.8142	0.6918	4.5158
PFDT/FB-Char -500	5.1	29.2	18.4	52.4	75.76	2.61	0.62	0.07	0.10	20.84	0.5893	1.1145	0.9792	6.8765
PFDT/FB-Char -600	4.1	23.5	24.2	52.3	89.69	2.10	0.69	0.08	0.31	7.14	0.6805	1.1451	1.1388	7.1341
PFDT/FB-Char -700	3.6	20.5	23.1	56.4	88.55	1.02	0.56	0.10	0.40	9.37	0.5986	1.1216	1.0803	7.4232
PFDT/FB-Char -800	3.2	18.6	23.7	57.7	92.30	0.53	0.45	0.11	0.27	6.34	0.4493	1.0948	0.9964	6.7806
PFDT/FB-Char -900	3.7	19.5	26.6	53.9	95.58	0.79	0.63	0.17	0.20	2.62	0.3737	1.0382	1.1053	7.9897

[a] volatile matter; [b] fixed carbon; [c] by difference

7.3 Char Yield and Properties of Char from Mallee Bark Pyrolysis

Figure 7-2 presents the char yields from the pyrolysis of raw biomass in various reactor systems as a function of temperature. Below 600 °C, char yields are strongly dependent upon the pyrolysis temperature. Increasing the pyrolysis temperature from 400 to 600 °C leads to a considerable reduction in char yields from ~36.5 to ~25.9, from ~31.3 to ~20.8, and from ~ 27.9 to ~17.9 wt% db for biomass pyrolysis in the fixed-bed, continuous feeding drop-tube/fixed-bed, and pulsed feeding drop-tube/fixed-bed reactors, respectively. A further increase in pyrolysis temperature over 600 °C leads to little change in the char yield. However, a significant decrease (~7.8% db) in the char yield is evident for biomass pyrolysis in type II experiments (i.e., pyrolysis in the drop-tube/fixed-bed configuration with continuous feeding) between 800 and 900 °C. This can be attributed to the continuous volatile–char interactions, leading to the so-called "self-gasification"[169, 170] between reactive agents, such as CO2 and H2O (generated from the inherent moisture in biomass and/or produced from pyrolysis), in volatiles and the nascent char on quartz frit. Indeed, the SEM images for the char-produced from type II experiments at 600 and 900 °C clearly demonstrate that significant gasification reactions have taken place on the surface of char produced at 900 °C, as evidenced by the eroded surface texture with small cavities and/or grooves (see Figure 7-3). It should be noted that such reactions would be negligible in type I experiments, because the volatiles (hence, the reactive agents within) produced under fixed-bed slow-heating conditions would have been swept out of the reactor below 600 °C. Similarly, such self-gasification reactions would proceed to a much less extent in type III experiments, where with pulsed feeding, the lengthy period for interactions between the nascent chars on the frit with volatiles generated from the pyrolysis of the next batch of biomass particles is absent.

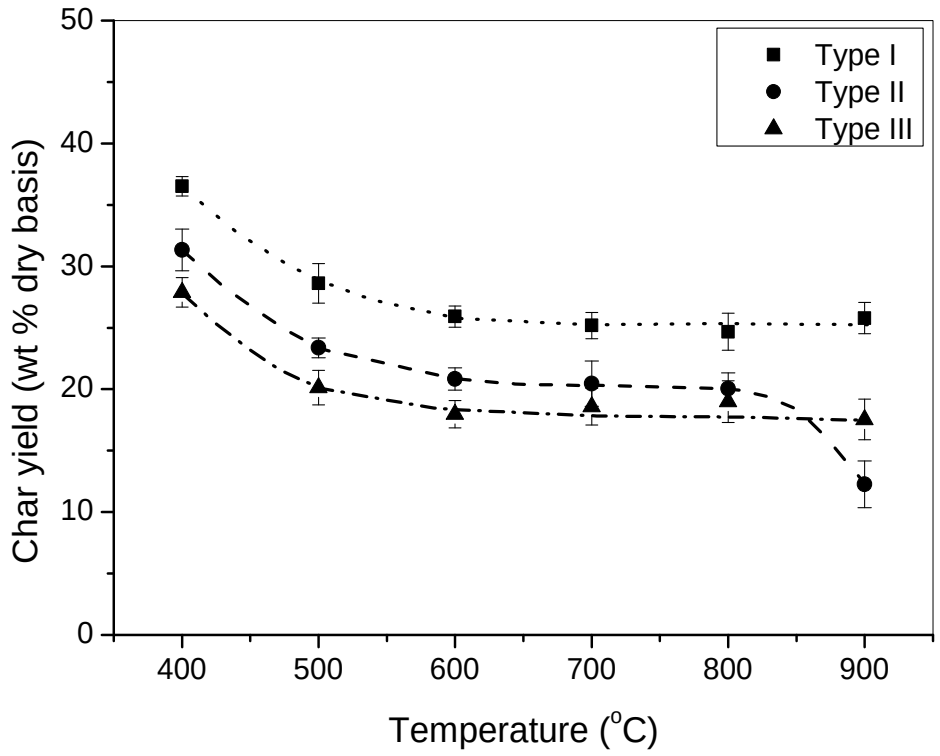

Figure 7-2: Char yields as a function of the temperature in three types of experiments: i.e., type I, pyrolysis in a fixed-bed reactor; type II, pyrolysis in a drop-tube/fixed-bed reactor with continuous feeding; and type III, pyrolysis in a drop-tube/fixed-bed reactor with pulsed feeding.

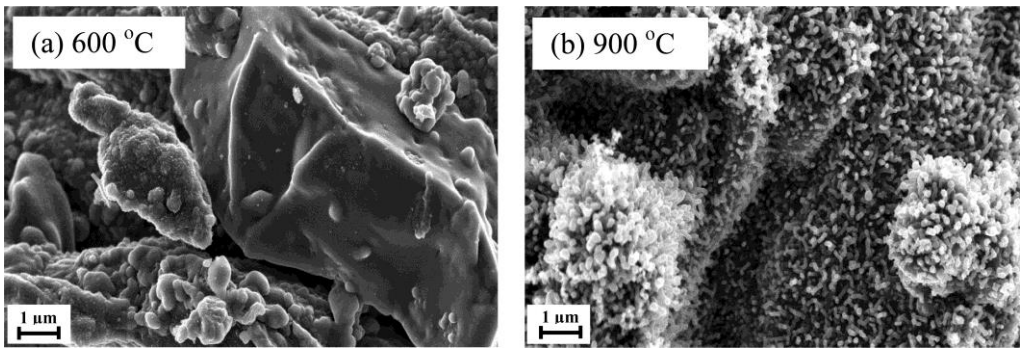

Figure 7-3: SEM images of char samples produced from pyrolysis in a drop-tube/fixed-bed reactor with continuous feeding at (a) 600 °C and (b) 900 °C.

As expected, Figure 7-2 shows that, at a given temperature, biomass pyrolysis in type I experiments (slow-heating pyrolysis in a fixed-bed reactor) has a higher char yield than those in type II and III experiments. At pyrolysis temperatures lower than

800 °C, at which self-gasification reactions are expected to be insignificant, char yields from biomass pyrolysis in type III experiments (fast-heating pyrolysis in the drop-tube/fixed-bed reactor with pulsed feeding) are lower than those in type II experiments (fast-heating pyrolysis in the drop-tube/fixed-bed reactor with continuous feeding). The data suggest that the lengthy and continuous volatile–char interactions in type II experiments also have produced coke, which deposits on the nascent char, leading to an increase in the char yield. Similar phenomena on coke formation were also reported previously during coal gasification[171] and biomass thermochemical conversions.[172, 173] Clearly, the results also, in turn, suggest that, upon volatile–char interactions, there are competitions between coke formation and nascent char "self-gasification", which becomes important at 800 °C or above.

The properties of chars produced from biomass pyrolysis under various conditions using different reactor systems are presented in Table 7-1, along with those of the raw biomass. As expected, the contents of ash and fixed carbon increased with the pyrolysis temperature, accompanied with a decrease in the content of volatile matter. Accordingly, the carbon content increased, while the contents of hydrogen and oxygen decreased with an increasing pyrolysis temperature. Table 7-1 clearly shows a significant discrepancy in the Cl content in chars produced under different conditions, indicating that Cl release is strongly dependent upon biomass pyrolysis conditions (to be discussed in the next section).

7.4 Release of Cl during Biomass Pyrolysis under Various Conditions

Figure 7-4 presents the data on the distribution of Cl in pyrolysis products (char, gas, and tar; see panels a, b, and c, respectively), along with Cl mass balance (see panels d–f) as a function of the pyrolysis temperature using different reactor systems. It should be noted that gas Cl is the water-soluble Cl (in ionic form, most likely as HCl[90, 92, 174] directly captured by the bubbler system, while tar Cl is calculated by difference. Therefore, tar Cl is mostly in the form of organically bound Cl in tar, which is water-insoluble.

In a fixed-bed reactor under slow-heating conditions (type I; see Figure 7-4a), little Cl is retained in char even at 400 °C. In other words, nearly all Cl species are released as part of volatiles (~23% as gas Cl and ~77% as tar Cl). Such a significant Cl release during pyrolysis at a temperature below 500 °C was also observed in previous studies for both other biomass fuels[19, 90, 92] and low-rank coal.[141] Further increasing the pyrolysis temperature up to 900 °C results in little change in Cl distribution (see Figure 7-4d) because of the "progressive nature" of slow pyrolysis; i.e., pyrolysis at 900 °C first experiences 400 °C, at which Cl would have been released. Conversely, Cl release follows a completely different trend in type II (i.e., pyrolysis in the drop-tube/fixed-bed reactor with continuous feeding) experiments, as shown in panels a–c and e of Figure 7-4. A considerably higher amount of Cl is retained in the char. Char Cl increases substantially with the temperature, from 0.8% at 400 °C to 44.1% 600 °C, coinciding with reductions in both tar Cl and gas Cl. This can be attributed to the recombination of Cl in volatiles into the char (with either an organic char matrix[141] or, more importantly, inherent metals,[175] such as AAEM species in char) as a result of the lengthy and continuous volatile–char interactions; such reactions appear to intensify as the temperature increases. Indeed, the data in Figure 7-5 show that, even at 600 °C, almost all of AAEM species in biomass are retained in the nascent char, providing an abundant source of such metals for Cl recombination. Furthermore, results from water leaching of the char produced at 600 °C also suggest ~ 90.2% of Cl in char being water-soluble as ionic chloride. A further increase in the pyrolysis temperature leads to a substantial reduction in char Cl, e.g., to 26% at 800 °C and 6% at 900 °C, clearly indicating that less thermally stable bonds between Cl in volatiles and nascent char can be formed as the temperature increases, leading to increases in tar Cl and gas Cl. These results are in agreement with the previous observations in brown coal pyrolysis in a fluidized-bed/fixed-bed reactor.[141] Likewise, volatile–char interactions also proceed but at a much less extent in type III experiments (i.e., fast pyrolysis in the drop-tube/fixed-bed reactor with pulsed feeding). Indeed, char Cl follows a similar

trend with much lower Cl retentions (see Figure 7-4a). It is also interesting to note that, at 400 °C, while no obvious differences are observed in char Cl (see Figure 7-4a), for all three types of pyrolysis, gas Cl (see Figure 7-4b) in type I experiments in a fixed-bed reactor is considerably higher than those in type II and III experiments under fast-pyrolysis conditions. This indicates that, under fast-heating conditions, the released gas Cl also appears to react with tar in volatiles, leading to a noticeable increase in tar Cl. It is surprising to note that, for type II experiments, a further increase in the temperature to 900 °C leads to a drastic increase of tar Cl, accompanied by the sharp decrease in char Cl, while no obvious changes were observed for gas Cl (see panels b and c of Figure 7-4). This is possibly due to the formation of alkali chloride salts in the gas phase and their subsequent reaction and/or deposition in the reaction system, thereby contributing to tar Cl. This will be discussed in section 7.5. Nevertheless, calculations based on the Cl balance in Figure 7-4 (see panel d–f) clearly suggest that substantial amounts (47–84%; see Figure 7-4c) of Cl can be present as tar Cl during biomass pyrolysis in the three types of experiments under various conditions.

As shown in Figure 7-5, the release of AAEM species follows trends that are completely different to Cl release, which was also reported previously[141] for the pyrolysis of other low-rank fuels. The release of Na and K commences from 700 °C and becomes significant at 800 and 900 °C. This can be attributed to the intensified interactions between volatiles and nascent char [99] as well as the increasing volatility of these species as the temperature increases. While following a similar trend, the release of K appears to be more difficult than Na, possibly because of the nature of K[90, 92] being more electropositive than Na and, hence, capable of forming intercalation compounds with carbons (hence, retained) in char.[176] Mg and Ca are divalent species and known to be difficult to release during pyrolysis because these species are heavier and of divalent bond with the char matrix, as suggested previously in a study on brown coal pyrolysis.[84] However, there is a small but appreciable increase in Mg and Ca release from 800 to 900 °C during pyrolysis in

type II experiments. This can be attributed to the lengthy and continuous volatile–char interactions under such conditions.

7.5 Direct Determination of Cl in Tar Under Various Conditions

As described in section 7.4, substantial amounts (47–84 wt%; see Figure 7-4c) of Cl may be present as tar Cl during biomass pyrolysis, depending upon the pyrolysis conditions. Direct combustion of Cl-containing volatiles (type IV experiment) produced from slow pyrolysis in the fixed-bed reactor and the fast pyrolysis with continuous feeding was conducted to quantify the total Cl present in tar. Such results are presented in Figure 7-6, along with the calculated data based on differences (from Figure 7-4) for benchmarking. As expected, for biomass pyrolysis in the fixed-bed reactor (at 400 and 900 °C), the combustion of Cl-containing volatiles achieves close to 100% Cl mass balance (see Figure 7-6a). This clearly demonstrates that, under the pyrolysis conditions, the majority of Cl is indeed organically bound in tar (i.e., tar Cl) and can be recovered after combustion. Similarly, close to 100% mass balance of Cl has also been achieved after the in situ combustion of volatiles produced from type II experiments under fast pyrolysis in the drop-tube/fixed-bed reactor with continuous feeding at 400 and 500 °C (see Figure 7-6b). However, as the pyrolysis temperature further increases, there is an enhanced reduction in the mass balance of Cl after volatile combustion. The results suggest that the in situ combustion of volatiles generated at higher temperatures cannot recover all Cl in the volatiles after combustion. In other words, part of Cl seems to be lost during the in situ combustion of volatiles.

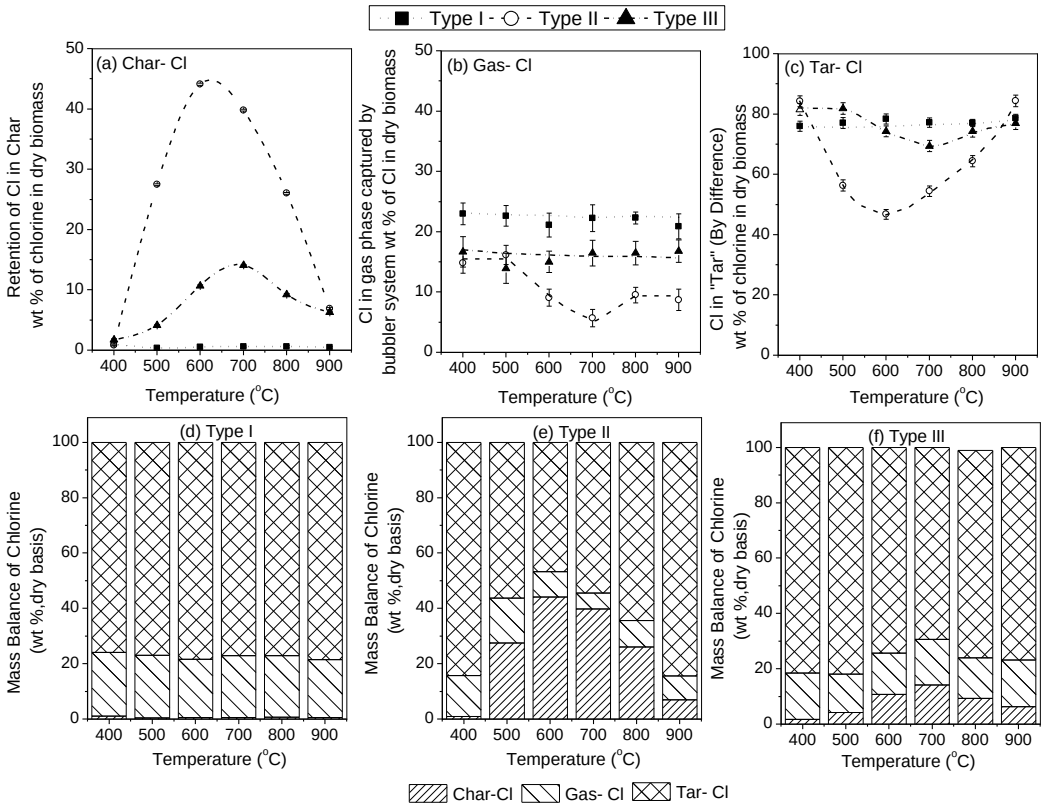

Figure 7-4: Distribution of Cl among (a) char, (b) gas, and (c) tar and mass balance of Cl during three types of pyrolysis experiments , including (d) type I (using a fixed-bed reactor), (e) type II (using a drop-tube/fixed-bed reactor with continuous feeding), and (f) type III (using a drop-tube/fixed-bed reactor with pulsed feeding). The mass balance of Cl is presented as the weight percent of total Cl in dry biomass. Cl in tar is calculated by difference from Cl in char and gas.

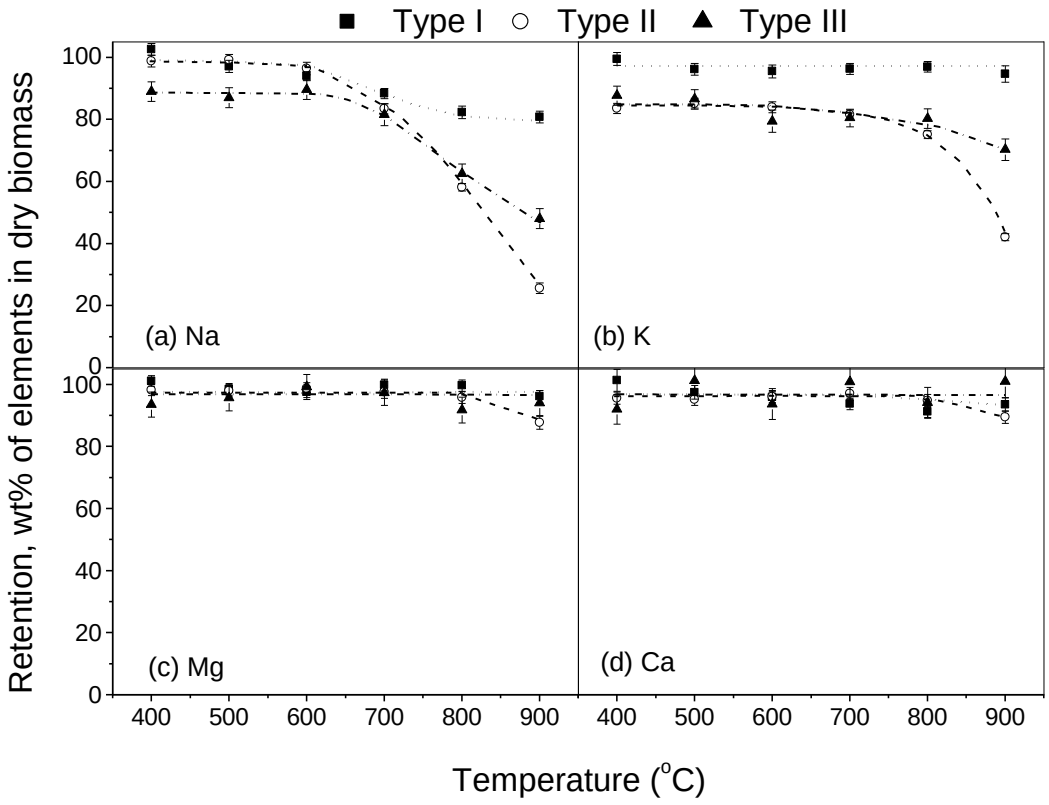

Figure 7-5: Retention of AAEM species in char produced from various types of biomass pyrolysis experiments, including type I (using a fixed-bed reactor), type II (using a drop-tube/fixed-bed reactor with continuous feeding), and type III (using a drop-tube/fixed-bed reactor with pulsed feeding).

The significant discrepancies observed in the Cl mass balance as presented in Figure 7-6b at high temperatures (>500 °C) appear to be related to the release behavior of AAEM species (particularly Na and K) during pyrolysis. Under the pyrolysis conditions (type II experiments using a drop-tube/fixed-bed reactor with continuous feeding), the data in Figure 7-5 show that the release of Na starts from 600 °C and increases substantially with a further increase in the pyrolysis temperature. While it is small (~10%) at low temperatures, the release of K starts to increase from 700 °C and accelerates with a further increase in the pyrolysis temperature. At 900 °C, the release of both Na and K are substantial, while the release of Mg and Ca are minimal. It should be noted that the in situ combustion of volatiles (generated from biomass pyrolysis in

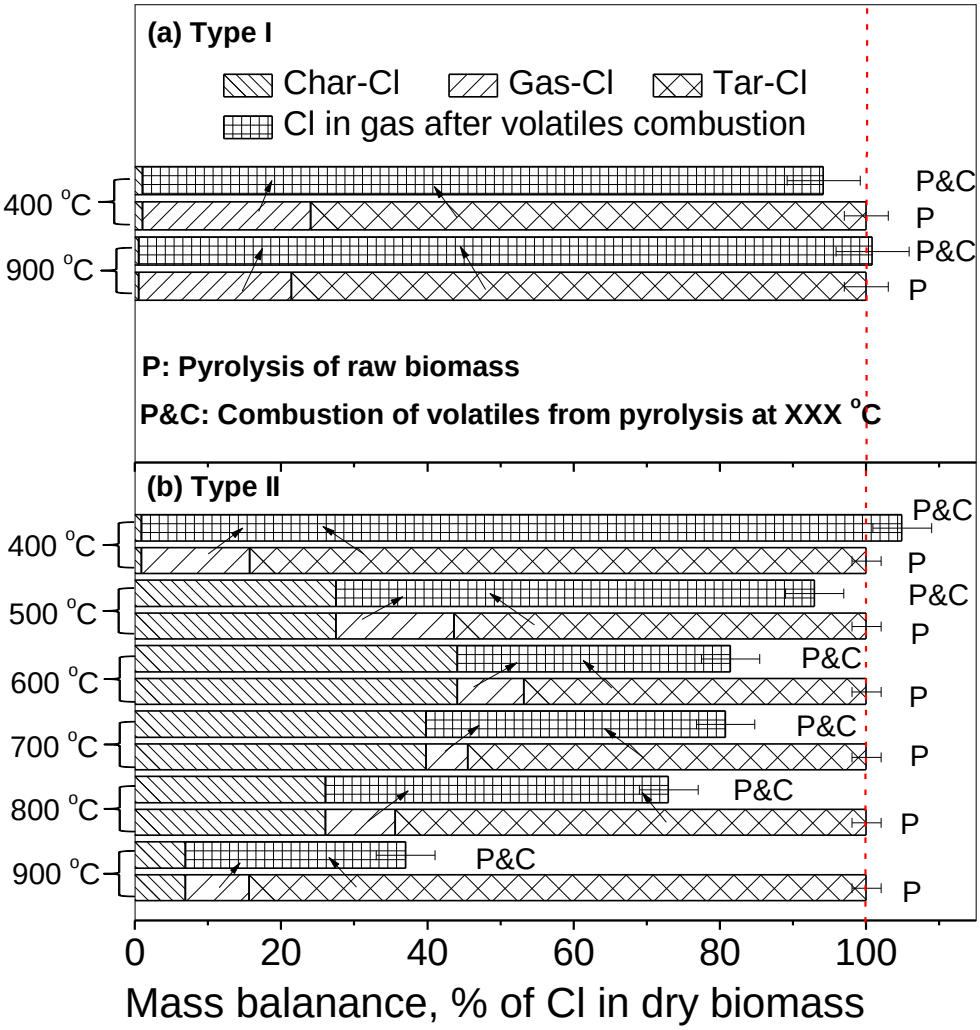

Figure 7-6: Mass balance of Cl from pyrolysis and combustion of volatiles produced in situ from raw biomass during different types of pyrolysis experiments, including type I (using a fixed-bed reactor) and type II (using a drop-tube/fixed-bed reactor with continuous feeding).

the drop-tube/fixed-bed reactor with continuous feeding) takes place at 950 °C. Therefore, the AAEM species (dominantly Na and K) would likely combine with the released Cl to form alkali chlorides via a series of gas-phase reactions during in situ volatile combustion. The formed alkali chlorides may react with the quartz reactor and/or deposit on the reactor surface, leading to substantial reduction in the Cl mass balance after volatile combustion. This is supported by the evidence (results

not shown here) that the combustion column became opaque after in situ combustion of volatiles and the observation of alkali and Cl in the EDS spectrum from the analysis of the internal surface of the broken piece of the reactor. Indeed, as shown in Figure 7-7, the molar ratio of (Na + K)/Cl in the volatiles increases substantially as the pyrolysis temperatures increases above 600 °C, indicating that more Na and K are available to react with Cl in the volatiles released during in situ combustion. It should also be noted that, when the pyrolysis was carried out under slow-heating conditions (the pyrolysis column is operated as a fixed-bed reactor), almost all Cl species (see Figure 7-4) were released at 400 °C, while nearly all AAEM species were retained in char (see Figure 7-5). Under such conditions, the opportunity for AAEM and Cl combination in volatiles during in situ combustion in the combustion column was limited, resulting in almost complete recovery of Cl present in tar after in situ combustion of volatiles.

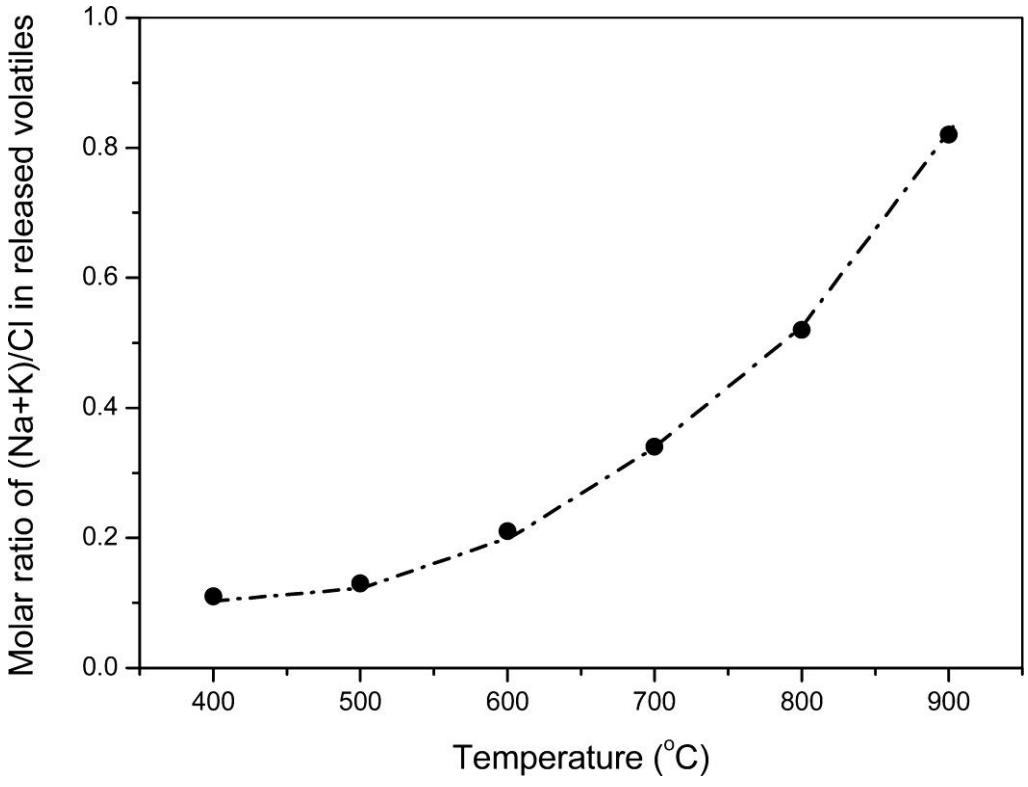

Figure 7-7 Molar ratio of (Na + K)/Cl in released volatiles during biomass pyrolysis in a drop-tube/fixed-bed reactor with continuous feeding.

7.6 Conclusion

This paper reports new data on the release of Cl and its distribution among char, tar, and gas during biomass pyrolysis under various conditions. All Cl in the raw biomass can be dissolved in water as ionic chloride. Little Cl was retained in char at a temperature as low as 400 °C under all reaction conditions. In a fixed-bed reactor, Cl release during biomass pyrolysis is insensitive to pyrolysis temperatures between 400 and 900 °C. In a drop-tube/fixed-bed reactor under continuous feeding, Cl retention in char increases as the pyrolysis temperature increases to 600 °C, at which Cl retention in char reaches a maximum of ~42% and then decreases to ~ 6% as the pyrolysis temperature further increases to 900 °C. Under pulsed feeding condition, similar trends (but to a much lesser extent) are observed for Cl release and distribution during biomass pyrolysis due to reduced volatile–char interactions and subsequent "self-gasification" between char and reactive gasification agents in volatiles at 900 °C. Calculations based on difference suggest that ~ 47–84 wt% of Cl is present in tars, depending upon pyrolysis conditions. Such findings were further confirmed experimentally via the quantification of Cl in tar using a two-column pyrolysis/combustion reactor, which burns the volatiles produced *in situ* from biomass pyrolysis and converts all Cl in volatiles into ionic forms, which are water-soluble for quantification. Furthermore, ~ 100% mass balance of Cl in char, tar, and gas can be achieved during biomass pyrolysis in a fixed-bed reactor at 400–900 °C or in the drop-tube/fixed-bed reactor below 600 °C. For volatiles produced from biomass pyrolysis in the drop-tube/fixed-bed reactor with continuous feeding at temperatures >600 °C, 100% Cl mass balance closure is not achievable because the volatiles contain abundant released inorganic species (Na and K), which appear to capture some Cl during *in situ* volatile combustion to form alkali chlorides deposited on the reactor wall.

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Introduction

This chapter summarizes key research achievements attained in this PhD studies. First major contribution is the development of two accurate universal methods for Cl quantification in coal, biomass and plastic based fuels. Secondly, this study give insights into Cl release behavior during the pyrolysis of NaCl loaded cellulose paving the way for better understanding Cl release behavior in biomass. Thirdly, it demonstrates the distribution of Cl in pyrolysis products of mallee biomass under various reactor configurations specifically highlighting the significance of volatile char interactions. Additionally, based on the understanding developed during the course of this study, recommendations for future works are given in this chapter.

8.2 Conclusions

8.2.1 Two-Step Method for the Quantification of Cl In Low-Rank Solid Fuels

- This work has developed a two-step method for the quantification of total Cl in low-rank solid fuels.
- The method has been validated by five standard samples and employed to quantify the total Cl in a bark, a brown coal, and a water-washed brown coal.
- Compared to the two-step method, the water-washing method yields similar result on the Cl content of the bark, in which Cl is present in water-soluble forms, but underestimates the Cl content of the brown coal samples due to the presence of water-insoluble Cl.
- While the conventional Eschka method can quantify the Cl content of the brown coal, it substantially underestimates the Cl content of the bark due to the Cl loss during Eschka combustion.
- Further investigation shows that in employing the two-step method, a

pyrolysis temperature of 500 °C is suggested, at which the Cl loss during volatiles in situ combustion and char Eschka combustion can be avoided.

8.2.2 Determination of Cl in Solid Fuels Using an Improved Eschka Method

- Both Two- step and Improved Eschka combustion methods are capable of accurately quantifying Cl in various solid fuels.
- The analytical time is shortened from ≥8 h for the two-step method to ≤3 h for the improved Eschka method.
- The other advantage is that the relative standard error (±2%) for the improved Eschka method is much smaller than that (±5%) of the two-step method.
- Eschka flux is capable of capturing all the Cl released as HCl (g) during the combustion of the mixture of Eschka flux and the mallee bark.
- Cl escaped with the flue gas during conventional Eschka combustion is not only in association with heavy unburned organic compounds but also in the forms of light organic compounds and/or gases (e.g., CH_3Cl).

8.2.3 Release of Cl from the Slow Pyrolysis of Nacl-Loaded Cellulose at Low Temperatures

- Cl is mainly released as HCl (g) from the slow pyrolysis of the NaCl-loaded cellulose at temperatures below 300 °C.
- Further increase in the pyrolysis temperature results in the release of Cl in the form of organically bound into tar (ie tar-Cl).
- The release of both HCl (g) and total Cl (including gaseous HCl and tar-Cl) commences at 200 °C, reaches the maximum at 350 °C, and then levels off with further increasing temperature to 400 °C.
- An increase in the pyrolysis temperature from 150 to 300 °C leads to a considerable increase in the amount of organically bound Cl in the solid

residues whereas further increasing temperature to 350−400 °C leads to its depletion in the solid residues.

8.2.4 Release of Cl During Mallee Bark Pyrolysis

- New data on the release of Cl and its distribution among char, tar, and gas during biomass pyrolysis under various conditions is presented.
- All Cl in the raw biomass can be dissolved in water as ionic chloride.
- Little Cl was retained in char at a temperature as low as 400 °C under all reaction conditions.
- In a fixed-bed reactor, Cl release during biomass pyrolysis is insensitive to pyrolysis temperatures between 400 and 900 °C.
- In a drop-tube/fixed-bed reactor under continuous feeding, Cl retention in char increases as the pyrolysis temperature increases to 600 °C, at which Cl retention in char reaches a maximum of ~ 42% and then decreases to ~ 6% as the pyrolysis temperature further increases to 900 °C.
- Under pulsed feeding condition, similar trends (but to a much lesser extent) are observed for Cl release and distribution during biomass pyrolysis due to reduced volatile–char interactions and subsequent "self-gasification" between char and reactive gasification agents in volatiles at 900 °C.
- Calculations based on difference suggest that 47–84 wt% of Cl is present in tars, depending upon pyrolysis conditions. It was confirmed experimentally via the quantification of Cl in tar using a two-column pyrolysis/combustion reactor, which burns the volatiles produced *in situ* from biomass pyrolysis and converts all Cl in volatiles into ionic forms, which are water-soluble for quantification.
- ~ 100% mass balance of Cl in char, tar, and gas can be achieved during

biomass pyrolysis in a fixed-bed reactor at 400–900 °C or in the drop-tube/fixed-bed reactor below 600 °C.

- For volatiles produced from biomass pyrolysis in the drop-tube/fixed-bed reactor with continuous feeding at temperatures >600 °C, 100% Cl mass balance closure is not achievable because the volatiles contain abundant released inorganic species (Na and K), which appear to capture some Cl during *in situ* volatile combustion to form alkali chlorides deposited on the reactor wall.

8.3 Recommendations

Further research suggestions are listed below

1. In order to understand the release behavior of Cl during biomass pyrolysis, studies on Cl release should be carried out on other components of biomass like lignin and hemicelluloses.

2. Kinetics of Cl release should be studied during biomass pyrolysis as it will give key information about the Cl release mechanisms.

3. Effect of reactor configuration on the release of CH_3Cl should be studied in order to develop understanding on the mechanisms governing CH_3Cl release.

4. Cl release during pyrolysis should be studied on leaf and wood samples.

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